

Proceedings of the 1990 EPA/A&WMA
International Symposium

**Measurement of Toxic and
Related Air Pollutants**

Jointly sponsored by the
U.S. Environmental Protection Agency's
Atmospheric Research and Exposure Assessment Laboratory
and the
Air & Waste Management Association

Technical Program Chairmen
R.K.M. Jayanty, Research Triangle Institute
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Measurement of Toxic and Related Air Pollutants

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Measurement of Toxic and Related Air Pollutants

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Preface

The 1990 EPA/AWMA International Symposium Measurement of Toxic and Related Air Pollutants sponsored by the Atmospheric Research and Exposure Assessment Laboratory of the U. S. Environmental Protection Agency at Research Triangle Park, North Carolina and co-sponsored by the Air and Waste Management Association of Pittsburgh, Pennsylvania was held May 1-4, 1990, at the Mission Valley Inn at Raleigh, North Carolina. The technical program consisted of 178 presentations held in 20 separate sessions. The sessions focused on recent advances in the measurement and monitoring of toxic and related pollutants found in the ambient, indoor, and source emissions atmospheres. New sessions were added this year to the symposium included: Radon, Atmospheric Chemistry and Fate of Toxic Pollutants, Super-critical Fluid Extraction, Determination of Polar Organic Compounds in Ambient Air, Mobile Sources Emissions Characterization, Effects of Air Toxics on Plants, and Air Pollution Dispersion Modelling. Session on Measurements of Volatile Organic Pollutants - Ambient Air focused on Long Path Spectroscopy and other methods of monitoring toxic pollutants. During the symposium over 70 exhibitors had booths displaying a wide range of pollution monitoring instrumentation and consulting services. Over 850 attendees from the U.S. and other countries attended the symposium. Contained in this volume are the papers presented during the symposium. The keynote address of Congressman David Price, Fourth District of North Carolina, presented by the Congressman's Administrative Assistant, Mr. Gene Conti, is also included.

Air pollution measurement and monitoring research are designed to support regulatory actions by developing an in-depth understanding of the nature and processes that impact health and the ecology, to provide innovative means of monitoring compliance with regulations and to evaluate efforts through the monitoring of long-term trends, and to anticipate potential environmental problems. The U.S. Environmental Protection Agency's Atmospheric Research and Exposure Assessment Laboratory at Research Triangle Park, North Carolina is responsible for research and development of new methods, techniques, and systems for detection, identification, and characterization of pollutants in emission sources and in indoor and ambient environments; for the implementation of a national quality assurance program for air pollution measurement systems; and supplying of technical support to Agency regulatory programs on local, regional, and global scale.

This was the 10th consecutive year the symposium was held and the 5th year of its co-sponsorship with AWMA. The objective of the symposium is to provide a forum for the exchange of ideas on recent advances for the reliable and accurate measurement and monitoring of toxic and related air pollutants in indoor, ambient, and source atmospheres. The ever growing number of presentations and attendees to this symposium represents advancements in the current measurement and monitoring capabilities.

Bruce W. Gay, Jr., (EPA)
R. K. M. Jayanty (RTI)
Technical Program Chairmen

ENVIRONMENTAL PROTECTION AGENCY INTERNATIONAL SYMPOSIUM
KEYNOTE ADDRESS - AIR TOXICS
REPRESENTATIVE DAVID E. PRICE
MAY 1, 1990

I'm honored to be able to present these remarks as the keynote to your conference today. I'd like to commend Drs. Jayanty, Gay, and Foley, and Mr. Kueser, as well as the Environmental Protection Agency and the Air and Waste Management Association for convening this annual symposium on toxic and related air pollutants.

We are proud to have EPA's air research facility headquartered in North Carolina and proud of our EPA scientists and the private sector companies which support EPA's efforts here, many of whom are constituents of this district. In my relatively short time in Congress, I have had the pleasure of working with EPA on several funding projects, including appropriations for a new EPA affiliated research lab in Chapel Hill and the hoped for acquisition of a supercomputer -- and, longer term, on a major new research facility in the Research Triangle Park. I value the close working relationship that we've developed and anticipate its continuation.

In my brief remarks this morning, I would like to provide a broad context for the environmental issues you will be discussing this week and to give you an overview of some specific legislative initiatives that will have an impact on your work in the years to come.

Around the globe, we are confronting serious environmental problems. Solving these problems will require a sustained research effort that can provide policy makers with reliable information. Over the last twenty years, EPA's research budget has declined more than 20% in real terms and more than 500 scientists have been cut from the agency's payroll. Yet during the same period, EPA's regulatory responsibilities have vastly increased through the enactment of major new statutes.

This pattern of neglect must be broken. You may be aware that the Congress is currently working on legislation to elevate the status of the Environmental Protection Agency. On March 28 of this year, the House passed legislation to redesignate the EPA as a cabinet level department. Similar legislation is awaiting floor action in the Senate. We believe a Cabinet-level EPA will help serve notice that we have made the environment an important national priority -- consistent with the status that environmental protection has reached in many countries around the world.

I was pleased to see President Bush submit a budget to Congress this year that includes an increase in federal air quality programs. The fiscal year 1991 budget request for air quality programs is \$390 million -- a \$100 million or a 35% increase over last year's funding level. Most of the increase would be targeted to State assistance activities to implement the provisions of a reauthorized and stronger Clean Air Act, but \$17 million will support more aggressive air research programs, including a \$9 million increase to address the specific issues of air toxics and non-attainment of National Ambient Air Quality Standards.

Funding for EPA, and virtually every other program within the federal budget, has been constrained in recent years, but there is still a tremendous reservoir of confidence and support in Congress for the work of EPA. This is not to say EPA can or should escape the scrutiny or the discipline that our current budgetary crisis requires. But a solid case can be made for research expenditures as a critical national investment, one that pays rich dividends in the health and well-being and security of our people and in the vitality of our research and educational institutions.

As we stand on the brink of a new year and a new decade, we look ahead to assess the critical issues of the 1990's. There are few issues as important -- to us and to our children -- as the protection of our global resources. A recent survey indicated that 90% of Americans say that "taking stronger actions to clean up the nation's air and water is a top priority for government and business leaders."

Even more dramatic evidence comes from data analyzing the willingness of the American public to pay for more environmental protection. In 1981, the public split about evenly on this question. By 1989, the public indicated a willingness to pay by a margin of about 4 to 1. There will be, of course, continuing discussion about how much people will have to pay but there is no mistaking the strong public commitment to a better environment.

The "greening of America" is taking place in Washington as well. Congress is paying a great deal of attention to environmental issues now, and -- perhaps more importantly -- we're working with an administration that recognizes the problem as well. We still have our differences with the White House -- witness several key votes on oil spill liability -- but the prospects for cooperation are far better than they were during the Reagan years.

With this broad background in mind, let me review some of the legislative action in the current session of the Congress. Clean Air legislation is the number one environmental issue before the Congress this year. Clean air legislation was put off by President Reagan and did not get addressed by committees of the Congress for the last decade because of an ongoing deadlock between those who wanted stricter pollution controls and those who wanted more lenient ones. However, the expiration of compliance deadlines under the 1977 amendments and heightened public concern about health and the environment almost certainly will result in the enactment of a strengthened version of the Clean Air Act this year. Earlier this spring, just prior to the Easter recess, clean air legislation took giant strides toward enactment, clearing the House Energy and Commerce Committee on a 42 to 1 vote and passing the Senate by a wide margin, 89 to 11. I expect floor action on the House version later this month.

In the meantime, the House Science, Space and Technology Committee, of which I am a member, has approved legislation to expand air pollution research under the Clean Air Act. Provisions in this legislation include expansion of research and development programs on the health effects of air pollution, as well as improving monitoring and control methods. This legislation will be offered as a floor amendment to the House version of the Clean Air Act. Such legislation should mean additional R&D dollars for North Carolina -- particularly the EPA lab in the Triangle. As you know, much of the nation's cutting-edge environmental research is being done here in the Triangle, and I will be pushing to commit adequate resources to these efforts. To do a better job of implementing environmental controls and environmental health policy, we need a solid base of scientific knowledge.

We are also seeing an increased emphasis on control of air toxics included in the House and Senate versions of the Clean Air Act. This effort will require stepped up research on your part if we are to rationally control these compounds.

It is extremely important to establish tougher standards for toxic air emissions. One major flaw of the 1970 Clean Air Act was the system established to regulate hazardous air

pollutants. In the nearly two decades since the Clean Air Act was enacted, EPA has only regulated seven pollutants. This pace is too slow -- uncontrolled air toxics pose substantial health risks and we must improve this regulatory process. I think we were all alarmed by the announcement EPA made in April of 1989 showing that manufacturing industries released 2.7 billion pounds of toxic air pollutants in 1987. Most observers, including EPA officials, expressed surprise at the volume of toxic releases and called them unacceptably high.

The essential questions that must be answered in this debate on air toxics revolve around two distinct issues. The first involves the distinction between point sources of pollution -- i.e., specific, large sources of toxics -- and area sources, which include the exhaust from our cars, the discharges from small businesses, and similar sources. The second involves the type of remedy we seek from these sources -- i.e., whether we impose specific technology-based solutions or whether we impose health-risk based solutions.

The President's clean air proposal required EPA to regulate only 50% of the major sources of hazardous air pollutants. During House committee consideration, an amendment was adopted that would require EPA to regulate all categories of major sources. The only exception to this rule, in the case of sources with carcinogenic emissions, is that EPA may exempt a source category from regulation if it determines that no source in the category presents a lifetime risk of cancer greater than 1 in 1 million to any person.

Data presented to Congress indicate that toxic emissions from area sources are collectively responsible for as many cancer cases as are emissions from point sources. Under the President's bill, regulation of these area sources was entirely discretionary. The amended House bill now requires EPA to regulate 90% of the area source emissions of each hazardous air pollutant. EPA may elect to establish controls based on "general available control technology" in lieu of the more stringent controls based on "maximum achievable control technology" that would apply to major sources.

The technology based standards required for major and area sources under the amendment may not eliminate all health risks from toxic emissions. To address the "residual risks" that may remain, the amendment requires EPA to report to Congress on legislative alternatives within ten years. If none are enacted at that point in time, the law would revert to the more stringent but thus far unenforced health-based standards of the 1977 Act. Although the Senate bill includes a second-stage health-based standard, the likely final product will be closer to the House bill language.

Another area of concern to members of Congress is the issue of indoor air pollution. People spend about 90% of their time indoors, and air contaminants commonly found in the home and workplace are known to cause a wide range of health effects. Public concern about the threat of indoor air pollution to human health and worker productivity has increased dramatically in the past two decades. Media reports about the "sick building" and "sick home" phenomena are now common.

Scientific information about the sources and effects of indoor air pollution is increasing steadily. At the same time, definitive conclusions about the health effects of indoor air pollution remain controversial. It is difficult to associate definitively a given response with a single air pollutant, in or out of doors, because many factors in the human environment can contribute to particular health conditions.

These issues were pursued during hearings before the Science, Space and Technology Subcommittee on Natural Resources, Agricultural Research and the Environment, last year. In response to these hearings, our subcommittee recently marked-up and reported H.R. 1530, the Indoor Air Quality Act. This legislation would strengthen EPA's indoor air research program; would promote development of health advisories to indicate levels at which identified contaminants would have no adverse health effect; would focus the use of existing regulatory authority to implement a national response plan based on the health advisories; would provide grants to the states to assist them in developing basic management strategies and assessments; would establish an EPA office for indoor air activities and a coordinating interagency Council on Indoor Air Quality; and would give EPA the lead responsibility for developing a federal response to indoor air quality.

A companion bill has been introduced in the Senate by Majority Leader George Mitchell and is pending consideration at the full committee level. I am hopeful we can enact this necessary legislation this year.

A large part of the indoor air pollution debate focuses on radon. EPA estimates that radon is responsible for 5,000 to 20,000 case of lung cancer each year. If these figures are accurate, radon may be the nation's leading radiation problem and the second largest cause of lung cancer. Recent studies, however, have challenged these health estimates and provide a stronger basis for continued research on this issue.

Federal statutory authority for dealing with the radon problem is not as clearly defined in existing law as it should be. The Superfund Reauthorization Act authorized an EPA radon gas and indoor air quality research program, including a national

assessment of radon gas and a demonstration program to test methods of reducing or eliminating radon. To support its Radon Action Program, EPA received \$12.4 million in fiscal year 1990. The President's budget requests \$13.7 million for FY1991, an increase of 11% from FY1990.

To address the increasing concern about the potential effects of radon, in the first session of the 101st Congress, 11 pieces of legislation related to radon issues were introduced. None have been enacted thus far. H.R. 1530, the Indoor Air Quality Act would address radon through a comprehensive indoor air quality approach. Several major policy issues remain to be addressed: which federal agency should deal with radon regulations?; is the EPA-recommended radon action level protective enough of human health?; and does scientific information support public concerns and the need for EPA guidelines? I would like to see these issues addressed by the Congress in the near future and encourage those of you working in this area to move forward aggressively with your research.

As you can see, our country is demonstrating increased awareness and concern about environmental quality; the public response to Earth Day leaves no doubt about that. And this concern is being translated into policy initiatives, shaking loose once-stalled items like oil spill liability and clean air and stimulating discussion and debate on the environmental agenda of the future -- matters ranging from rain forest destruction to ozone depletion to global warming to alternative energy sources. No one is more aware than you how critical a part research will play in determining the extent of the dangers and what solutions we can feasibly pursue. We're also aware that research -- an honest facing of what our best scientists tell us -- will not always or even usually be comforting. The need for research must not be a rationalization for inaction. On the contrary, as you are in a better position than most to know, for this country and the world community to make good on the lofty pronouncements of Earth Day, it is going to require strong leadership, considerable sacrifice, major commitments of resources, and much determination in the years ahead. What is going on here at EPA and other research facilities gives me great hope that we can rise to the challenge, a challenge that should transcend everyday politics.

Through these research efforts, we're investing in our future, in the healthy future of our children and the well-being of generations to come. I want to commend each of you for the part you are already playing in that and to thank you once again for the opportunity to participate in this symposium.

FUTURE NEEDS IN RADON MONITORING

Introductory Remarks on Radon
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Indoor radon monitoring is currently dominated by charcoal adsorption devices for short term monitoring and alpha track devices for long term monitoring. Several other devices are also available. The simplest is an electrical device which allows radon to be read with a special voltmeter. The most complicated are delicate instruments requiring a skilled operator. This paper discusses the radon measurements which will be needed in the future and develops the measurement device characteristics necessary to fulfill these future needs. The available radon monitoring methods are evaluated with respect to their ability to satisfy this set of future needs.

Introduction

The Environmental Protection Agency believes that a large fraction of the U. S. population is exposed to unacceptable risk from radon and has advised everyone with significant exposure potential to test their home. Unfortunately, only a small fraction of homes have been tested, and many people believe the complicated nature of the radon testing process is partially to blame for this poor response. EPA suggests a two step testing process; first a screening test is used to decide whether a problem might exist in the house, then a long-term follow up test is used to measure the radon exposure of the residents. Few people seem willing to go through this testing process, which usually takes more than a year. This testing scheme also is not well suited to radon testing during real estate transactions. A simpler and shorter testing scheme will probably be needed for residential testing. Some means will be needed to relate this short term testing to the average exposure of the residents. The main change in radon monitoring foreseen by this author is an increased reliance on short term tests.

Schools and offices pose special testing problems because they are unoccupied a large fraction of the time. Heating and air conditioning systems are frequently shut down or cut back during this unoccupied time, which can produce substantially different radon concentrations. This must be accounted for if radon exposures in these buildings are to be accurately assessed. It has also been observed that the working level ratio is significantly lower in large buildings than in houses. Where 4 pCi/l yields about 0.02 WL in houses, it may yield only .004 WL in large buildings.

Most radon testing today is performed using charcoal adsorption or alpha track devices, though many other monitoring methods are available. The charcoal devices are limited to short monitoring periods and are well suited to the screening measurements currently recommended by EPA. Alpha track devices are well suited to the long term follow up measurements. The remainder of this paper is devoted to a discussion of future monitoring needs. The suitability of today's monitoring methods to these needs will be discussed.

The "Ideal Radon Monitor"

The ideal radon monitor may not be possible with today's technology. It is also possible that there may be conflicting requirements for different applications. No one radon monitor will necessarily be ideal for all purposes. The attributes of the "ideal" radon monitor are given below.

Accuracy

The radon monitor should accurately measure the radon. Accuracy limits of plus or minus 25 percent have been used by EPA

for the Radon Monitoring Proficiency (RMP) program. This level of accuracy does not reflect the limits of radon monitoring technology. It was chosen to reflect the degree of certainty of the radon risk estimates. It also accounts for the fact that radon itself is variable and any measurement can only reflect the radon at the time the measurement is made. While most methods can yield better accuracies with careful procedures, a few laboratories have difficulty in meeting the 25 percent error limit in double blind tests near 4 pCi/l.

Minimum Measurable Concentration

EPA has set an action level of 4 pCi/l as an indoor average radon concentration. The Indoor Radon Abatement Act sets a national goal that indoor radon be as low as outdoors, and requires EPA to review its action level. In response, the action level may be revised in the near future. No decision has been made on future level at the time of this writing. It is possible that a radon concentration different from 4 pCi/l could be chosen. It is also possible that it would be based on something other than an annual average concentration in the living areas of the house. Different action levels may be chosen for different applications such as schools. It may be necessary to accurately measure radon concentrations below 4 pCi/l to reach this goal.

Sampling Time

While it is desirable to be able to measure radon over a period of a year, it appears that most radon mitigation decisions are being made based on much shorter tests. A full year of testing is prohibitive in a real estate transaction. Most people who monitor out of concern for their health base their actions on short term tests. An analysis of radon variability has shown that the minimum sampling time for a reliable test is one day, and that errors decrease as sampling time is increased to two days. There is a small additional improvement for sampling times of a week. Beyond this time, little additional accuracy is gained until sampling times become impractical to serve the purpose of the test. An ideal sampling time of two days to a week is selected for use here. The radon monitor should be able to measure within 25 percent at 4 pCi/l over a 2 to 7 day period. Sample time should be in multiples of one day to avoid diurnal variations in radon.

True Average

The radon monitor should provide a true average radon concentration over the sampling time. If, for example, the device is heavily biased toward the last day of the sampling period, then this is effectively a one-day sample and is subject to the variability associated with one-day measurements.

Storage Capability

The device should not need immediate analysis. If a large number of samplers are returned to a laboratory for analysis at one time, the lab must be able to process them within the time that a useful measurement can be made. Devices which store radon for future counting are subject to radon decay. Half the radon collected is lost every 3.8 days. A delay of a month reduces the radon available for counting by a factor of 250.

Sensitivity to Environment

The measurement method should not be sensitive to normal variations in temperature or humidity or other common environmental parameters. Ideally, there should be quantitative limits for this sensitivity, but for purposes of this paper, we will require that common environmental parameters not cause errors beyond the allowable accuracy limits at the minimum measurable concentration.

Calibration of Active Devices

The device should remain in calibration for at least six months and preferably as long as a year. Recalibration should be a relatively easy. It should be possible to make a performance check without transporting the device to a radon chamber.

Operator Skill

The required level of operator skill should be kept to a minimum. College level mathematics should not be required in order to operate the device.

Cost

Cost should be kept to a minimum. Current costs for charcoal and alpha track tests ranges from about \$10 to \$30. The cost per test should not be greater than the high end of this range.

Proper Pollutant

There are two basic measurements, radon and radon decay product. The decay products will not occur in a constant ratio to the radon concentration. The ratio will depending on the age of the air being sampled, the amount of air movement and the presence of any filtration. In addition, some decay products will be attached to dust particles, while others will be unattached. While decay products are responsible for the bulk of radon's health effects, the variables in decay product measurement make it difficult to do a health assessment based on a typical short term decay product measurement. This is because of the variability of decay product concentrations. On the other

hand, radon is the pollutant entering the building, so if one wishes to know the effectiveness of a radon mitigation, radon is the appropriate parameter to measure. In choosing whether to measure radon or its decay products, it is important to have a clear understanding of the purpose of the measurement and to control those factors which could influence the measurement.

Intermittent Sampling

Buildings with intermittent occupancy, such as schools and office buildings, may best be sampled only during hours of occupancy, especially if ventilating systems are also operated intermittently. This could result in significantly different radon concentrations when the building is not occupied. The measurement should be able to differentiate between these periods in some way, or its usefulness may be limited in this context.

Anti-tampering

As radon becomes a factor in real estate transfers, it might be expected that radon testing will become more common in this situation. In this circumstance, the party selling the house (and usually occupying it at the time of the measurement) has an economic stake in the outcome of the test. There is an incentive to cheat. Radon tests need to be structured to prevent tampering, either by the design of the test device or through some external controls.

Conclusions

Many radon and decay product monitors are available which give a wide range of costs and capabilities. No one monitor can do every job, and each is suited to a different application. In the future, the author expects an increased reliance on short term tests, so methods which are good only for long time periods will probably enjoy less success. This is apparently being anticipated by the equipment manufacturers because the methods are being adapted to shorter sampling times. The short term alpha track detector is a good example of this.

The shortening of the sampling period will also allow greater use of the more equipment intensive methods. Where it would not be cost effective to leave a continuous radon or working level monitor in place for several months to a year, placing it for a day or two will probably be practical. Thus the use of continuous monitors is likely to increase. These devices are also particularly well suited to schools and offices where occupancy is intermittent and where ventilation systems are often cut back for weekends and evenings. These devices are really the only way to accurately assess what is happening. Their increased cost may also be better afforded by the institutions involved, but this is heavily dependent on how many rooms must be sampled. Perhaps the best strategy will be continuous monitors in one or two locations and inexpensive samplers elsewhere. The

differences in working level ratios in large buildings also suggest that working levels as well as radon be monitored in these buildings.

For monitoring of homes, the driving force for testing increasingly seems to be real estate transactions. The trend appears to be toward samplers placed by professionals, at least for real estate purposes. Professionals have a great deal of flexibility in their choice of sampling method and are able to use skilled technicians. This segment of the testing market might be expected to grow in the future. The professionals can be expected to purchase the instruments that work for them and that give them a competitive advantage. It is likely that the larger operators would have several methods at their disposal and use whichever is best for the job at hand, or in combination as the need arises.

Many homeowners testing for their own information still seem to prefer to be able to buy a sampler at a local store. The local mail order market might be expected to remain stable, and seems to be the province of the charcoal and alpha track devices.

Prediction of Long-Term Average
Radon Concentrations in Houses
Based on Short-Term Measurements

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Previous studies have examined the relationship between short term screening tests and annual average radon concentrations, but have generally been limited by short term measurements conducted at only one location in the house or during only one season. This study examines the usefulness of short term measurements to estimate long-term averages when the short term measurements are made in living areas of the house in and in the basement. The effect of season is also examined. This analysis is particularly useful in situations where there is not time to do an annual measurement, but multiple rooms can be easily tested. We used the raw data from five different researchers to cover the full annual cycle and multiple sampling locations. The result is a matrix of factors which can be used to estimate the annual average radon based on a test at any time of year. Separate factors are calculated for basement and first floor monitoring locations.

Introduction

The Environmental protection Agency Published the Citizen's Guide to Radon in August of 1986. The Citizen's Guide outlines a two-step testing process which calls for an initial screening measurement followed by a longer term follow-up measurement. If radon in excess of four picoCuries per liter is detected by the screening test, additional tests of up to a year's duration are recommended. The whole measurement process including the time needed for the test, purchase of detectors, sample analysis, mailing, and procrastination can take well in excess of a year.

Under some circumstances, a full year of monitoring is not practical or is not desired by the person conducting the test. In this circumstance it would be desirable to be able to compare the short term test with the concentration that would have been measured if a full year test had been conducted. Five existing data bases have been collected and analyzed. These data bases were selected because there were both short term and long term tests performed in the same house. In addition, houses where continuous monitoring has been conducted have been used to investigate the variations in testing accuracy which result from different sampling durations. The results suggest corrections can be made to short term data to provide an estimate of long term averages in houses. This paper uses radon measurements made in several thousand houses to derive factors which can be used to normalize short term radon data to whole house annual averages.

Use of a short term sample to estimate the annual average can be expected to introduce additional error into the radon measurement process. If the errors that are introduced are smaller than those inherent in the measurements, the additional errors would be unimportant. If, however, the errors introduced by short term sampling are larger than the measurement errors, then there will be the need for a policy decision on whether or not these errors are acceptable. That decision is beyond the scope of this paper, but we will attempt to quantify the errors.

Optimization should be an inherent part of this process. The decision on the acceptability of errors should not be based purely on the errors observed from simple comparison of short term measurements with annual averages. These short term samples will include variance due to seasonal differences, location differences and differences due to house conditions as well as "random" variations. Many of these sources of variance can be reduced by the prudent choice of sampling strategy and application of correction factors. When the estimate is as good as can be made from the available data, then the decision on whether or not the errors are acceptable should be made.

Experimental Methods

Five independent datasets were used in this analysis. These are the first year data from the EPA State surveys, Data

collected by George Mason University for a survey in Northern Virginia, data collected by Pennsylvania in the Reading Prong, continuous radon monitoring at one location in each of four houses in Butte, Montana and continuous radon monitoring at several locations in a house in Media, Pennsylvania conducted under the auspices of Rutgers University. The original data was obtained to allow a consistent analysis to be performed.

No new radon measurements were made for this investigation. Because existing radon data was used, the author was limited to whatever analytical methods and quality assurance procedures were used by the person who collected the data. These ranged from carefully calibrated quasi-continuous radon monitors to radon test kits purchased on the open market. All radon measurements were assumed to be accurate, i.e. there was no systematic bias. Precision was accounted for by eliminating measurements known to be of low precision. For example, alpha track detectors bought in the marketplace were assumed to have usable precision only above a 1-year average of one pCi/l. This is well above the limit of detection for these detectors, and typically yields a coefficient of variation of about 20 percent (equivalent to 4 pCi/l for 3 months). Charcoal detectors of many types were also included in this analysis. These were again assumed to be unbiased. This assumption is supported by the analysis of data collected by Mose. Short term samples using three different charcoal detectors were shown to be unbiased estimators of alpha track averages at the same location when the lower radon concentrations were eliminated. The EPA/State survey data was of high quality because of careful quality assurance procedures.

The parameter of interest in this investigation is the ratio of a short term measurement to a long-term average. This requires that the short-term to long-term ratio is not a function of radon concentration. This independence is shown by Perritt. There is a noticeable decrease in precision at low concentrations, which may account for a dependence being seen by others. The long term average chosen here as a baseline was the average of radon concentrations in all floors of the house. This is not the same as the EPA follow up protocols which exclude space that is not actually lived in. This was done because the "lived in" status of floors of a house was generally not reported in the data, and because the utilization of rooms in a house is not a property of the house. A basement that is not lived in this year may have a couch and a television in it next year. All "livable" spaces were therefore assumed to be occupied.

Results

The EPA/State survey provides seasonal short-term to whole house annual ratios for winter and spring. The George Mason University data contains useful seasonal information for summer and fall but lacks sufficient measurements to calculate a whole house average. The adjustment of the George Mason University data was done by normalizing to the EPA/State data. The spring

season is contained in both datasets and so the George Mason University seasonal factors were adjusted to make the spring ratios the same as those from the EPA/State dataset. This adjustment is intended to yield "whole house averages" from other seasons of the George Mason data.

Both the Pennsylvania and New York data allow direct comparison of winter and annual data. Floor-to-floor differences can be examined in the New York and Pennsylvania data, but there is insufficient data to directly calculate whole house averages because of the lack of second floor measurements. It is not clear whether the houses had second floors that were not measured or if second floors did not exist. This leads to the dilemma whether to compensate for the lack of second floor data in calculating a household average. We have elected to make this small correction as if second floors existed in all houses.

From the table below it can be seen that summer first floor radon measurements should yield a result close to the whole house average, while similar winter first floor measurements should be higher than the whole house average by a factor of 1.6. Summer basement measurements should yield results about 1.8 times the whole house annual average while basement winter measurements should be 2.4 times the whole house annual average. Note that this data is unbalanced. The overestimation in winter is not balanced by an underestimation in summer. The basement overestimation is not accompanied by a first floor underestimation. The author believes this is due to the inherent bias in the screening locations and in the closed house conditions used for the short term tests. The annual averages include periods of low radon concentration which were "designed out" of the short term tests by choice of sampling location and closed house conditions. Note the similarity among the datasets.

	winter	spring	summer	fall
Basement Seasonal (closed house) to Whole House Annual				
EPA/State	2.9	2.1		
Geo. Mason	2.3	2.1	1.8	2.3
Pennsylvania	2.0			
Average	2.4	2.1	1.8	2.3
First Floor Seasonal (closed house) to Whole House Annual				
EPA/State	2.2	1.3		
Geo. Mason	1.6	1.3	1.1	1.5
Pennsylvania	1.5			
New York	1.2			
Average	1.6	1.3	1.1	1.5

Another source of variance is the inability of a short term sample to predict a long term concentration. We investigated this effect by breaking continuous monitoring data in five houses into simulated short term samples. With uncontrolled house conditions the 95 percent confidence limits yielded a range from 1.4 times the average to 0.1 times the average. This variability

can be considerably reduced by avoiding summer sampling, or presumably by sampling under closed house conditions. When summer samples are eliminated the range is from 1.4 to 0.7 times the annual average. This reduction in variance is accompanied by the introduction of a systematic overestimation in the radon concentration by about 10 percent. If one wished the most accurate prediction, it would be prudent to remove this bias. On the other hand it may be decided that such a bias is desirable in that it reduced the chance of under-estimating the radon. There appears to be a small improvement in predictive ability as sample time is increased from one day to about one week, with little additional gain in accuracy until large fractions of a year are sampled.

Conclusions

We have shown that short term sampling can provide estimates of long term radon concentrations at the same location with little bias. However there is considerable variance associated with the ability of individual samples to predict a whole house average. The variance is partly due to the differences between houses, partly due to differences between floors in a house, partly due to the time when the short term sample was taken and also due to other random effects. If short term measurements are to be used to predict a long term whole house average, then this variance should be reduced to a minimum. Any procedure which can be incorporated into a sampling protocol which reduces the variance is desirable.

The variance can be reduced by a number of techniques. For example there is a systematic difference between the radon measured in the basements and first floors of houses. It is possible to compensate for the systematic difference by applying a correction based on our experience with large numbers of houses. Further reduction in variance is possible if sampling is done simultaneously on more than one floor. By sampling in this way, it is no longer necessary to estimate the floor to floor differences based on a large number of houses. The differences become known, at least at the time of the sample. This should reduce the variance in the resulting prediction. In addition the number of floors is not the same in all houses. A house with a second floor has twice the chance for non-basement radon exposures as a one story house. One would calculate a different whole house average for a two-story house than for a ranch house. The number of floors in a house are easily counted, so there is no reason to treat all houses as if they were of one design. The author therefore recommends sampling on each floor of the house as a means of minimizing the errors in the calculated average.

It may also be possible to use the simultaneous basement and first floor measurements as a confirmatory measurement. If floor to floor differences fall outside an expected range, then the measurements may be suspect. Basement to first floor ratios

appear to fall mainly in a range from 1 to 4 from the New York and Pennsylvania data. Thus if one were to make short term measurements in a basement and on the first floor and the ratio were between one and four, the data would seem credible. In the data examined this ratio appears to fall outside these limits about 25 percent of the time. A ratio of .75 to 5 is satisfied about 85 percent of the time, so less "rejections" of tests can be obtained by using wider limits. The ratio between basement and first floor tests be used as a quality assurance tool with limits of 1 to 4 or .75 to 5 depending on the level of confidence desired.

By prudent choice of sample duration and house conditions, it is possible to minimize the variance due to sample time. It has been shown that closed house samples of about a week duration can generally predict average radon levels at the same location within about -25 to +40 percent (the bias due to closed house conditions.) This suggests that any sampling protocol should include closed house conditions and that the duration of short term samples be more than a day and preferably as long as a week.

Seasonal variations were also obvious in the data. These seasonal variations are a source of variance if a short term measurement is to be used to predict an annual average. Unlike floor to floor differences, seasonal variations in a particular house cannot be determined except by actually measuring the radon in more than one season. It will therefore be necessary to utilize seasonal trends from large numbers of houses to reduce this source of variance. It cannot be eliminated because of the differences between houses in their seasonal radon patterns, but at least the seasonal trends can be removed.

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AN ANALYSIS OF THE PARAMETERS INFLUENCING RADON VARIATIONS IN A HOUSE

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The purpose of this study was to devise a statistical means of eliminating interfering variables from data of specific interest. The primary data being sought were the comparative differences in radon concentration in a residential dwelling under two operating modes.

Radon levels were measured in the basement, the first floor, and the second floor of the house. A meteorological station was constructed that continuously measured the variable parameters such as wind speed, wind direction, outside temperature, relative humidity, and barometric pressure. The operating modes were changed every two weeks and the data were examined in two-week cycles.

An attempt was made to remove the effects of the unwanted variables by using the standard stepwise linear regression. Since this approach was not adequate without compromising the quality of the data of primary interest, a novel time-scale method was developed to achieve the desired discrimination. This utilized a computer routine to simulate the effect of an electronic RC filter.

When the averages were taken for comparison of the effect of change on radon concentration in two operating modes, they were seen to be separated by 15 standard deviations. Thus, this new method of variance reduction, by removing the unwanted time scales, yields results that are clearly significant.

A residential dwelling in a rural area near Media, Pennsylvania, was the site for a recent radon study that encompassed a five-month period of continuous meteorological and radon data collection. The home, a five-year old, two story, colonial wood frame structure, with standard insulation and a full basement, was modified with an apparatus to observe the effect of the radon levels in the dwelling when the modification was switched on and off. Previous observations, though limited in scope, showed radon levels in the basement to range between 15-20 pCi/l.

A rigorous statistical analysis was performed on each of the data sets. Initial efforts focused on assessing whether the raw data showed a normal distribution by applying the Chi-square test. If the data were not normally distributed, various numerical transformations were applied as appropriate, to try and obtain a normal distribution, e.g., a 24-hour moving average (smoothing function), log transformation, or other numerical corrections associated with an observed phenomenon, for which there is a known or logical explanation.

Since the data generated are time-based, i.e., they represent a time series which may have cyclical characteristics. When such a trend exists -- described by the correlation of radon (dependent variable) with barometric pressure, temperature, and other associated factors -- the trend may be removed by subtracting it (slope of the line generated by performing a linear regression) from the original data set. Otherwise, the opportunity to detect any difference in the mean values of the radon concentrations may be masked by unwanted variation, especially if the difference is numerically very small between the mean radon values representing the two operating modes.

When time series data are analyzed, one must account for the tendency of each measured value of a parameter to depend in some way on the previous values of that parameter. This dependence can occur in two ways. For physical systems which cannot change instantaneously, the physical state of the system at time t can best be represented by its state at time $t - \Delta t$, where Δt , is an increment of time. As Δt approaches zero, the value of the parameter, $F(t)$, approaches its value an instant ago, $F(t - \Delta t)$. Auto-correlation of the time series provides a measure of this effect, with Δt used as a displacement in time. The decrease in autocorrelation as Δt increases provides a measure of how fast the parameter can change. Some time series also exhibit periodic or cyclical variations. These variations are usually superimposed on random variations in the system (and the measurement). In this case the autocorrelation will initially decrease as Δt is increased, and then level off somewhat or even increase as Δt approaches the period of the cycle.

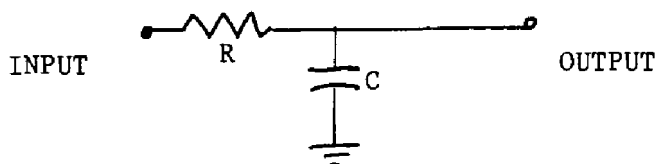
When a long time series, such as several months of weather data are analyzed, there will be a number of components to the time series. Ambient temperature provides a good example of this. First, there will be a tendency of each temperature measurement to depend on the previous temperature. There will also be a cyclical variation with a period of one day reflecting the periodic nature of the driving force, sunlight. This will be superimposed on a variation with a time scale of a few days as weather systems move across the measurement device. Finally, there will be an annual cycle with a period of one year. These variations can be represented in the frequency domain using a Fourier transformation, and the result is a power spectrum.

If one desires to determine the effect of one variable on another, for example, the effect of temperature on radon, variance can be reduced by choosing the time scale of interest and excluding variations which occur on greatly different time scales. For example, when changes happening on a two-week scale are being examined, variations on an annual or a daily time scale are of little interest. These variations contribute to the variance in the data without adding useful information. This can best be illustrated by graphic examination of the data. It can be seen that both radon and temperature exhibit diurnal effects. This does not imply cause and effect because household activities unrelated to outdoor temperature can affect radon. At this point it must be decided whether these 24-hour variations are central to the analysis of cause and effect, or if they are more likely to introduce artifacts. In this case diurnal variations are more likely to

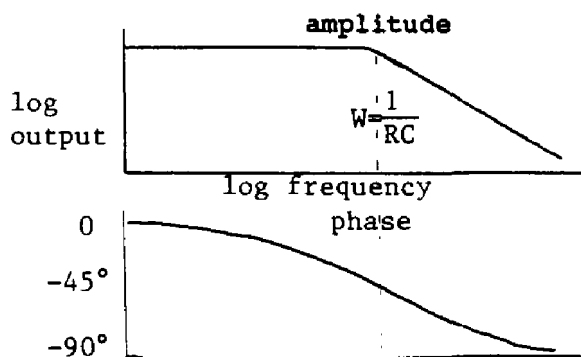
introduce artifacts, and so they would be removed. One easy way to remove these diurnal variations is to apply a transformation. The simplest way to do this is to take a moving 24-hour average of the data. This removes variations not of interest which reduces the likelihood of artifacts in the analysis. This also reduces the variance in the data thereby improving our ability to identify more subtle effects.

After diurnal variations are removed, it can be seen that in the short term radon seems to increase as temperature increases. On the other hand, the annual cycle, part of which can be seen in the data, shows radon going down in the summer as temperature rises. These two opposite effects tend to cancel when the time series are correlated. If the true relation between the variables is to be investigated, it is necessary to analyze each time scale independently. There is a need to transform the data in some way to isolate time scales of interest in much the same way that diurnal variations were removed.

It is possible to construct a mathematical filter to select the time scale of interest. This may be accomplished relatively easily by making an analogy to an electrical circuit. A resistor and capacitor provide a simple filter to select a frequency range of interest. The electrical circuit diagram appears below.



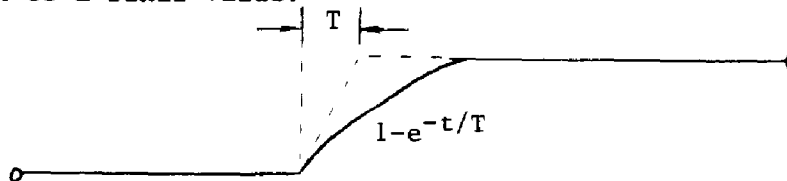
The response of this filter can best be represented by a plot of the output level versus frequency. This is done on log-log coordinates and is called a Bode plot. The circuit above yields close to 100% response (output equals input) for very low frequencies. For high frequencies, output decreases with increasing frequency. As frequency is doubled, response is halved. There is a critical frequency where the response transitions from flat to frequency dependent. This critical frequency, in radians per second, equals $1/RC$. Angular frequency in radians per second is cycles per second times two pi. A Bode plot of the simple RC filter above is shown below.



Note that a phase change is introduced by the RC filter. For frequencies above $1/RC$, there is a 90 degree phase shift. At $1/RC$ the shift is 45 degrees. Only at frequencies well below $1/RC$ is the output in phase with the input. This is important in selecting the filter constants since this phase change may appear as a time shift in the data near $1/RC$. In order to utilize this filter in analysis of data it is important to consider both the amplitude and phase of the response. Properly used, such a filter will allow variations with angular frequencies slower than $1/RC$ to pass while attenuating those above. This low-pass filter can be very useful in observing long term trends and variations in the data. It may also be used to remove these long term trends by simply isolating them and subtracting them from the input. This effectively produces a high-pass filter.

The above paragraphs describe the desired response of the filter. A practical realization of this transfer function may be formulated by taking advantage of the fact that the response of an electrical circuit to a step input in the time domain uniquely defines the frequency response of the filter. If one desires to construct a function which responds in the frequency domain as an RC filter, it is only necessary to construct a filter with the same response to a step input. This is what is done below.

In response to a unit step input, i.e., an input which suddenly changes from zero to one at time t a simple low pass RC filter produces a response of the form $1 - e^{-t/T}$ where T is a time constant equal to the product of the resistance and capacitance, RC . This is the same RC used above for the critical frequency in the Bode plot. This function is graphed below and is a simple exponential approach to a final value.



A useful property of this function is that the slope of the output function at any point on the curve is tangent to a line which intercepts the final value at $t+T$. This property arises from the fact that

$$d/dx(e^x) = e^x$$

By simply producing a formula that does this, the desired filter can be created.

Let $F(t)$ be the input function's present value and $G(t)$ be the output function's present value. At time t this function must be changing at a rate which would cause $G(t)$ to intercept input function $F(t)$ at time $t+T$. The slope of $G(t)$ must therefore be $(F(t) - G(t))/T$. In discrete mathematics, $G(t+1)$ may be calculated by simply adding the slope to $G(t)$. Hence the output at any given time is $G(t+1) = G(t) + (F(t) - G(t))/T$. This function is used directly in the Lotus spreadsheet. Choice of T allows the filter function to be tailored to the desired response, with the critical angular frequency being $1/T$.

Consistent with the analytical plan, observed radon values (raw data spikes were adjusted, i.e., attenuated to compensate for concurrent rain events that clearly affect radon levels. Other factors that also appeared to contribute to abnormal basement radon values, e.g., windows or doors remaining open for extended periods of time, were analyzed using daily log information, and to the extent necessary, appropriate adjustments were made on the initial radon values, by performing a linear interpolation.

The raw temperature data were plotted against time, for the entire monitoring period. Examination of the graphical representation showed a mild concave-up trend line for the period, a trend that was expected, due to seasonal changes, but a trend that could hamper the analysis and opportunity to see any difference between the two study modes. This long-term trend, was successfully removed by employing the electrical analog filtering technique, previously described.

At this point, each of the data sets namely, outside temperature, relative humidity, barometric pressure, and wind were subjected to a Chi-square analysis, to determine if each of the full period (November through March) meteorological data sets, and, in particular, the now modified (rain-corrected) basement radon data, satisfy a normal frequency distribution. Basement radon values were found to be normally distributed after transforming the data, i.e., doing a 24-hour moving average, and then performing a log transformation. In light of the observed benefit, the remaining data sets were also modified using the moving average technique. However, the remaining meteorological parameters did not satisfy a normal distribution, even though various transformations were applied to the data. Of the four parameters analyzed, only the barometric pressure data came

sufficiently close to being characterized as normally distributed, after performing a 24-hour moving average data transformation. In light of the above findings, it became evident that further statistical analysis of the data and associated results should be viewed with a certain degree of caution. A truly valid comparative statistical analysis, requires that each data set has similar frequency distributions, e.g., normal frequency distribution.

After all the data sets were transformed (smoothed), to remove any diurnal variations - daily and seasonal variations were not the center of interest - a series of statistical correlations (regressions) was performed on each of the meteorological parameters, relative to the log-transformed, normally distributed, basement radon data. This was done to prepare the data for the correction (removal) of trends generally associated with time series data, trends that could mask the possibility of observing any difference--particularly if the difference is very small--in radon levels between the two study modes. Each of the regression analysis-generated slope and y-intercept values, with the values for m and b respectively, in the linear equation, $y = mx + b$, for the line that best fits the data being studied, and the coefficient of correlation.

To illustrate:

let Y = Radon Initial Value, at Time T ,
 X = Barometric Pressure Initial Value, at Time T ,
 Y_1 = New Radon Value, at Time T ,
where, m = Slope of Line (Trend)
 and, b = y - Intercept
then, $Y_1 = Y - (mX + b)$.

These corrections were applied even if the correlation (slope of the trend line) was low, and no plausible explanation could be offered or established, to explain the relationship between the independent (meteorological) and dependent (radon) variables. Two iterations were required to perform this phase of the analysis.

The first iteration generated the following correlation (r value), and in descending order of priority:

* Barometric Pressure ----- 0.44
* Relative Humidity ----- 0.37
* Wind (E-W Vector)----- 0.28
* Temperature ----- 0.14

A second correlation analysis was done after the data sets were shifted in time, specifically in three-hour increments, forward and backward from their initial and corresponding (time dependent) values, until a maximum correlation (r value) could be found. It yielded the following correlation values:

* Barometric Pressure ----- 0.54
* Relative Humidity ----- 0.39
* Temperature ----- 0.36
* Wind (E-W Vector) ----- 0.28

Consistent with the above findings and planned method of analysis, the trend (relationship) between barometric pressure and the parameter having the highest correlation value with radon was removed. The revised basement radon values were again subjected to a third correlation analysis, with the remaining meteorological data sets, namely, relative humidity, temperature and wind.

Three more basement radon corrections were executed to remove the trends, correlations--observed above, i.e., temperature, relative humidity and wind. In each case, the last revised basement radon value was used in the adjustment process. Revised basement radon values and corresponding meteorological parameters were then subjected to a second regression analysis, after each trend correction was made to confirm that the adjusted slope of the trend line (correlation) was indeed zero.

Basement radon values were then graphically plotted versus time. Although considerable effort was expended to carefully filter out--to the extent possible--the unwanted (trends) variations, diurnal and seasonal bias, within the observed basement radon variation--again presumed to be due to meteorological influences--a concave-down (semi-cyclical) wave was observed which presented yet another unknown influencing factor. This finding called for the reuse of the trend-filtering technique, previously described.

At this point the adjusted basement radon data listed in a continuous time series format, were split into two numerical groupings. One group, representing basement radon readings for the bi-weekly periods, when the dwelling operated under the first study mode. The second group represented basement radon values, when the dwelling operated under the second study mode. The data, were then subjected to an analysis of variance to see if there was a statistical difference in basement radon values between the two operating modes. It showed that the differences between the means was over 15 times the standard deviation of the means and therefore the differences were very significant.

Application of Building Diagnostic Techniques to Mitigate Very High Radon
Levels in a Commercial Building on a Superfund Site

by

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ABSTRACT

A small commercial facility built upon a minerals extraction plant process waste fill was found to have average radon daughter concentrations of 0.4 working levels (WL) with peak concentrations exceeding 2.0 WL. At the request of EPA's Region 8 Emergency Response Branch, the Office of Research and Development's Air and Energy Engineering Research Laboratory/Radon Mitigation Branch undertook and completed the mitigation of this building within 1 week after receipt of the request for assistance. The structure had been built in four stages which meant that two interior footings probably existed. Soil gas concentrations varied between 20,000 and 250,000 picocuries per liter (pCi/L)*. Pressure field extension testing, developed in residential and school mitigation, indicated that at least two suction points would be needed to successfully apply sub-slab depressurization to the building. Since radon levels were so high, each of the three slab sections was penetrated and depressurized with two sharing one suction fan. This system has maintained, for at least 38 days, average concentrations of 0.0075 WL which is well below the 40CFR192 (1) standard of 0.020 WL.

(*) 1 pCi/L = 37 Bq/cu m

INTRODUCTION

During the summer of 1989 a remedial investigation was conducted at a major contaminated property which is part of the Denver Radium Superfund Site, one of the original entries on the National Priorities List of uncontrolled hazardous waste sites. The property is an inactive chemical processing plant for the extraction and purification of reagent-grade metals. Many years before, in the 1917-1924 era, the plant had been the site of a small radium extraction facility where ore containing radium and other naturally occurring radioactive materials was brought by train from western Colorado and subsequently purified for various uses. The waste products from this operation remained largely forgotten on the property, mixed by the activities of wind, water, and humans, until 1980 when they were discovered as a part of a major radioactive waste investigation.

In the course of the remedial investigation, properties adjacent to the existing chemical processing facility were checked to determine whether any radioactive contamination had migrated beyond the present-day property boundaries. Elevated gamma radiation exposure rates were identified in and around a small, one-story office building due east and across a street from the processing facility. With the cooperation of the building's owner, substantially elevated gamma radiation levels and radon (^{222}Rn) decay product concentrations were measured within the office building. Since the investigation had been conducted by a contractor for the Colorado Department of Health (CDH), and since CDH lacked the resources to deal with an emergency situation of this type, EPA was contacted and assistance was requested. Confirmation measurements were quickly made, and additional ventilation was instituted to bring the radon decay product concentration to less critical levels. Initial grab samples showed up to 4 working levels (WL, a special unit of radon decay product concentration) in the front office, which may be compared to the average allowable concentration in a uranium mine of 0.3 WL, set by the Mine Safety and Health Administration (MSHA) of the Department of Labor. MSHA also allows a maximum of only 1 WL before closing a mine or requiring worker respiratory protection. The initial ventilation measures reduced the average value to about 0.3 WL.

Having temporarily decreased the radon levels to a more reasonable if not satisfactory range, EPA examined the options for providing a more positive control mechanism. While there were several administrative possibilities to deal with this situation, it was decided to use the emergency response authority given to EPA under CERCLA/SARA (Comprehensive Environmental Response, Compensation and Liability Act/Superfund Amendments and Reauthorization Act) to install a radon mitigation system in the building. In this way it was possible to use some existing

contractual arrangements to proceed rapidly with the system design and installation. The EPA Region 8 Emergency Response Branch in Denver contacted the ORD's Radon Mitigation Branch in North Carolina. Through an existing contract with a Denver radon mitigation firm, ORD was able to bring the necessary equipment, supplies, expertise, and manpower to the scene within 1 week. Diagnostic tests were conducted and a complete radon control system was installed within a few days with minimum disruption to the building's occupants.

PREMITIGATION TESTING

Testing on this building began with charcoal canisters placed in the major office areas for 1 day followed by a repeat lasting 2 days. A gamma scan was performed at the same time. The data are shown on the building schematic in figure 1. Grab samples of radon and radon progeny taken at the same time agreed with the canister data. The radon progeny levels were far above the accepted 0.020 WL, with the range between 0.13 and 4.0 WL and the equilibrium ratio averaging 25%. These elevated levels triggered a more intensive investigation.

Continuous working level and radon gas monitors were installed in one of the offices. Even with the windows left open to reduce the exposure levels, the average progeny concentration was 0.25 WL (100 pCi/L @25% equilibrium) with diurnal variations between 0.012 and 1.0 WL. These data confirmed that a serious situation existed and it was decided to mitigate the building under the emergency response provisions of SARA.

BUILDING DIAGNOSTIC TESTING

Building diagnostics are performed to provide the necessary data to design a mitigation system. The building was evidently constructed in four stages. The slab was divided into a front slab which included the bathroom and secretary's area, a middle section containing the original office and the first added office, and a rear slab with an office and storage area (figure 1). The diagnostics attempt to determine the flow characteristics and the source strength of soil gas under the slab. Small holes were drilled in the floor in each room and a continuous sample of filtered soil gas was pumped into a Pylon AB-5 radon monitor which measures scintillation activity of the alpha decay events within the detection cell. Counts were printed out every 30 seconds and the levels noted when a steady reading was reached in 3-4 minutes. The concentrations of radon in soil gas under the floor slab were estimated to range from 33,000 to 250,000 pCi/L which are significantly elevated over typical background values and are quite consistent with the elevated levels of airborne radon found in the building. One soil sample obtained from beneath the slab showed a radium (226-Ra) concentration of about 3700 pCi/g, which may be

compared to 1-2 pCi/g found in normal soil, or to 15 pCi/g which is the maximum allowable concentration remaining at reclaimed uranium tailings sites.

With the extremely high levels found under the slab, extra safety measures were necessary. All building diagnostic and mitigation work was performed after normal business hours to limit possible exposure to the building's occupants. Full face masks using certified breathing air from pressurized tanks were used whenever penetrations were open in the slab. Protective overalls were available to reduce exposure to progeny deposited on skin and clothes.

The gas flow under the slab is investigated to determine if sub-slab depressurization can be applied to the building and the distance from which a single suction hole can pull soil gas. This test is called a pressure field extension measurement and uses a vacuum cleaner to apply a suction to a hole drilled at the site of a potential mitigation suction point and a number of small holes at varying distances from the suction point to determine how far a negative pressure can be detected. Potential suction points are selected after examining available blueprints and visual building inspection to determine if sub-slab barriers such as interior footings or sewer pipes exist. This building had no prints available, but the visual inspection indicated three or four different construction activities. A test suction point was located in each of three sections. The data indicated small pressure communication (less than 0.003 in. water or 0.75 Pa) between the center and rear office sections but none with the front reception area.

Because of the extremely high radon levels observed in this building, a conservative mitigation strategy was adopted. It was decided to locate a suction point in each section of the building, since the degree of sub-slab soil gas interconnection was not strong. The two suction points in the center and rear sections were connected to a common suction fan, while the one in the front section was connected to a separate fan. Following common mitigation practice, a hemispherical pit approximately 1-foot (30-cm) in radius was excavated under each 5-inch (12.5-cm) suction point hole cut through the concrete floor slab. This procedure minimizes the high pressure drop experienced as gas velocity through the soil increases near the hole and extends the distance the pressure field reaches. The fans were mounted outside the building so if any leaks developed in the pipe the suction in the pipe would pull room air in rather than inject soil gas back into the building. A vertical mounting was selected for the fans to allow any condensation to drain back under the slab and not collect in the piping or fan and freeze in the winter.

RESULTS

The effect of the mitigation system can be seen dramatically in figure 2. During the week prior to mitigation activities, the concentration ranged from 0.006 to 1 WL with the average about 0.2 WL. Mitigation activities caused a momentary increase as high as 2 WL, but when the fans commenced operation, the levels quickly dropped to less than 0.01 WL and were very stable. The average level over the next 38 days was 0.0075 WL, well below the accepted EPA guideline of 0.02 WL. Subsequent testing with passive radon monitors over the winter showed only minor seasonal increases in that level, indicating that the radon concentrations within the building have been successfully reduced and controlled. The gamma radiation exposure rates in the building remain elevated, however, and this will be dealt with in future remedial activities at this property. The building continues to be used by the occupants on a regular basis.

REFERENCES

1. Code of Federal Regulations. 40CFR192.

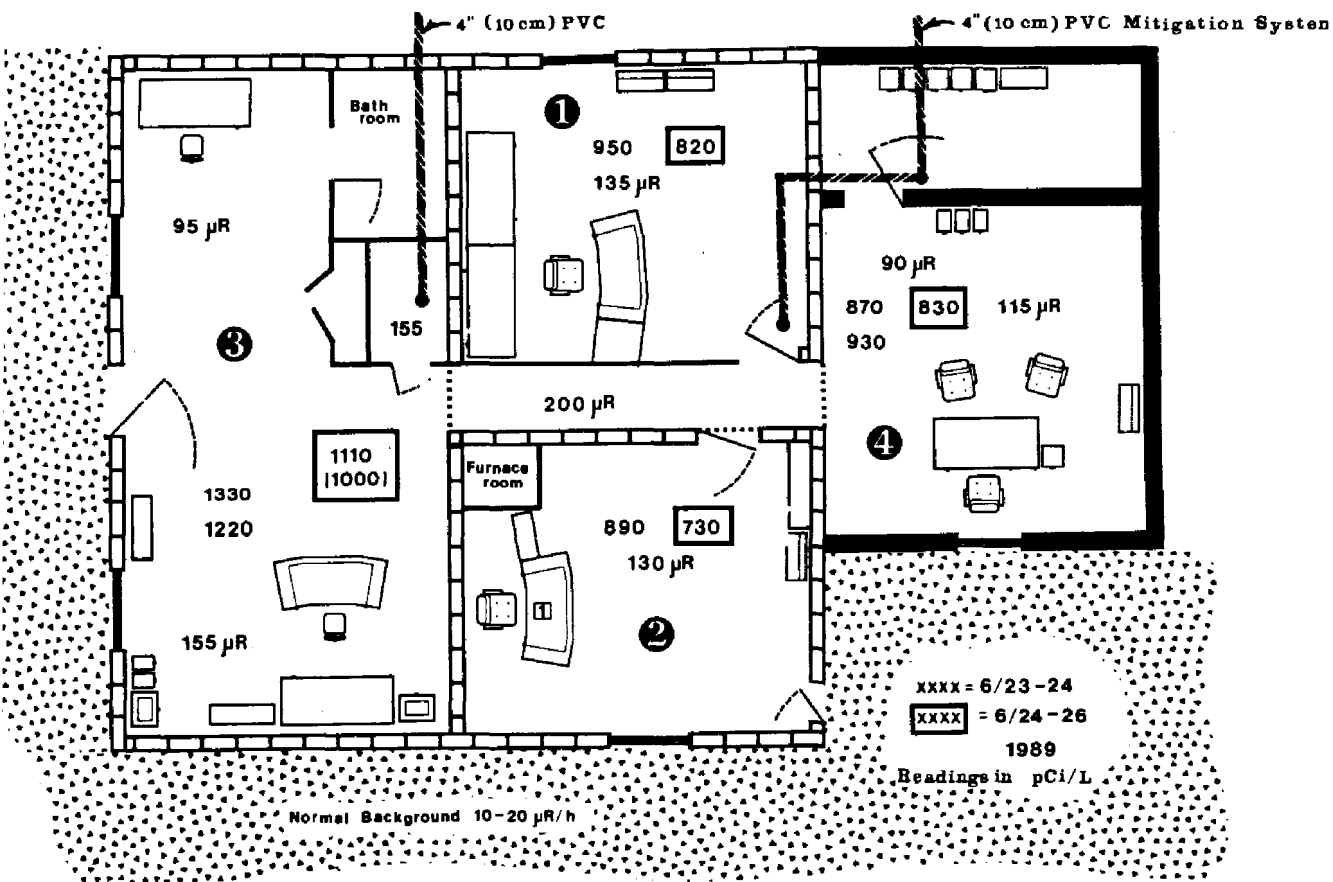


FIGURE 1.- Radon concentrations (pCi/L) and gamma readings (μ R/h)

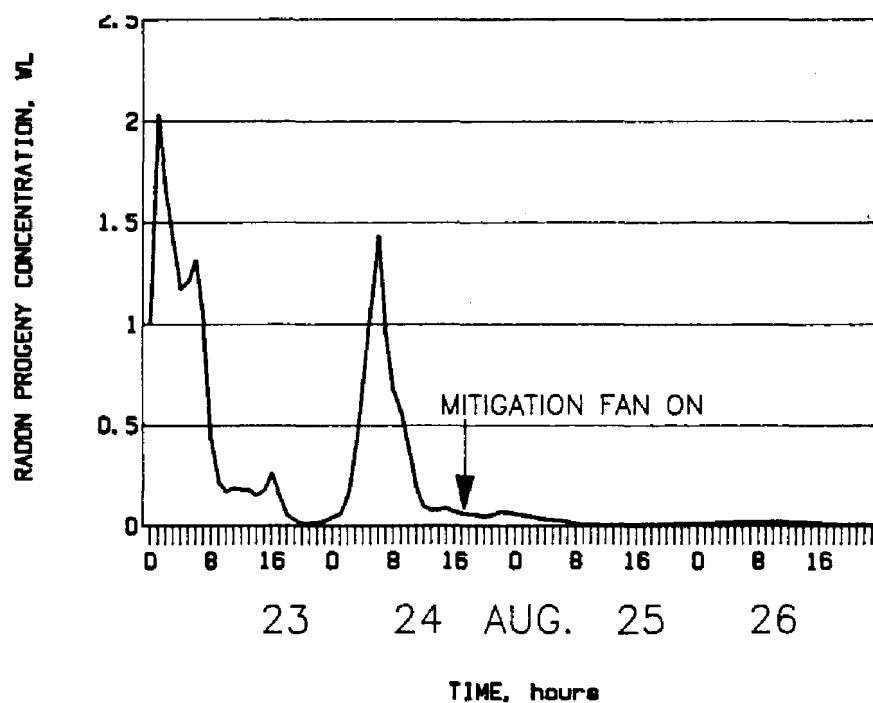


FIGURE 2. Radon progeny levels during and after mitigation

**AN AUTOMATED, SEMI-CONTINUOUS SYSTEM
FOR MEASURING INDOOR RADON PROGENY
ACTIVITY-WEIGHTED SIZE DISTRIBUTIONS,
 D_p : 0.5-500 NM**

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A system for the detection and measurement of indoor radon progeny activity-weighted size distributions (particle size, $d_p > 0.5$ nm) and concentration levels has been developed. The system is microcomputer-controlled and involves a combination of multiple wire screen (Graded Screen Array) sampler-detector units operated in parallel. The radioactivity sampled in these units permits the estimation of the radon progeny activity-weighted size distributions and concentration levels on a semi-continuous basis. This paper presents details of the system and describes various stages in the development of the system. Results of field measurements in a residential environment are presented to illustrate the resolution, sensitivity and capabilities of the measurement system.

INTRODUCTION

A substantial interest in the properties and occurrence of radon and its progeny has arisen in recent years from the recognition that the infiltration of radon into the indoor environment may constitute a significant human health hazard. The inhalation and subsequent lung deposition of the short-lived radon progeny, ^{218}Po , ^{214}Pb , and $^{214}\text{Bi}/^{214}\text{Po}$, have thus warranted the study of their diffusivity and association with molecular cluster aerosols in the ultrafine cluster size range (0.5-5 nm) and to larger mode aerosols.

Traditionally, the ultrafine cluster and accumulation modes of the activity size distribution have been termed as the "unattached" and "attached" fractions, respectively, in view of the significant difference in their diffusivities. "Unattached" ^{218}Po has been assumed to have a single, constant diffusion coefficient, typically $0.054 \text{ cm}^2/\text{sec}$ (1), and samplers have been developed that provide operationally defined estimates of these two modes of activity (9). Experimental measurements of activity-weighted size distributions in recent years have shown that the "unattached" fraction is in reality an ultrafine cluster fraction in the 0.5-5 nm range, whose diffusivity and characteristics are dependent upon the nature of the indoor atmospheric environment (4,10,11).

In view of the important contribution of the ultrafine cluster mode to the estimated lung alpha dose (e.g., 5), efforts have been made to develop size distribution measurement techniques that overcome the lack of sensitivity of conventional methods for particle size, $d_p < 5 \text{ nm}$. The alternative techniques developed have been adaptations of the wire screen diffusion battery concept, and have been called Graded Screen Arrays (GSA) (4,8). GSA systems consist of varying mesh number, single/multiple wire screen stages operated either in series or in parallel, with a choice of a wide range of wire screen parameters and sampling flow rates, coupled with a technique for the determination of the radioactivity associated with the particle size distribution.

GSA systems can be classified into grab sampling (4,8) and simultaneous sampling/analysis categories (11,13). The conceptual design of the automated, semi-continuous GSA system described in this paper thus evolved from an attempt to utilize the most advantageous features of both of these systems (6). The primary objective of the system was to provide semi-continuous estimates of ^{218}Po , ^{214}Pb , and ^{214}Bi activity size distributions and concentrations. The system was also required to be capable of adequate size resolution and sensitivity at low indoor radioactivity levels, and be experimentally characterized for ultrafine cluster diffusional deposition (plateout) losses. The development of the system is described in detail (8). The salient features of these developmental stages and results of recent initial field measurements are presented in this paper.

MEASUREMENT SYSTEM

The measurement system involves the use of 6 compact sampler-detector units (Figure 1) operated in parallel. Each sampler-detector unit couples wire screen penetration, filter collection and activity detection in a way as to minimize depositional losses while being sufficiently rugged for field operations. The system samples air simultaneously in all of the units through the sampler slit between the detector and filter sections in each unit (Figure 1). The filter section consists of a filter holder assembly that is inserted from the base of the lower aluminum block and allows easy filter replacement. However, in the initial design and field experiments, the filter holder assembly was sealed into the lower block. The sampled air is drawn through a 25 mm Millipore ($0.8 \mu\text{m}$ Type AA) filter that is supported by a stainless steel support screen. One of the sampler-detector units is operated with an uncovered sampler slit, thus providing information on the total ambient radon progeny concentrations. The sampler slits on the remaining units are covered with single or multiple wire screens of differing wire mesh number.

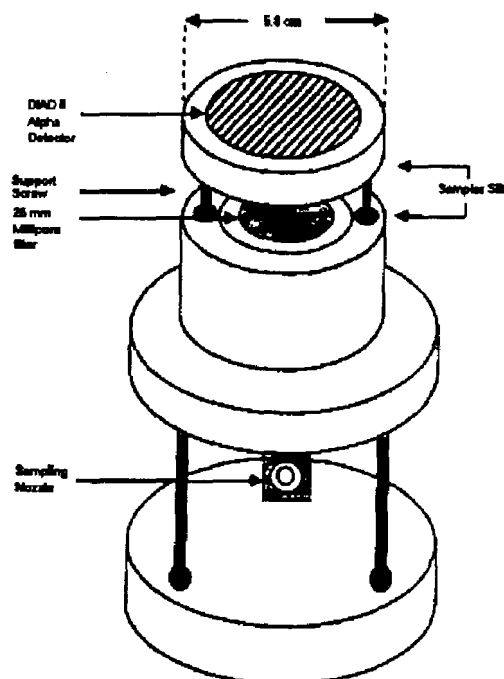


Figure 1. Sampler-detector unit in the measurement system.

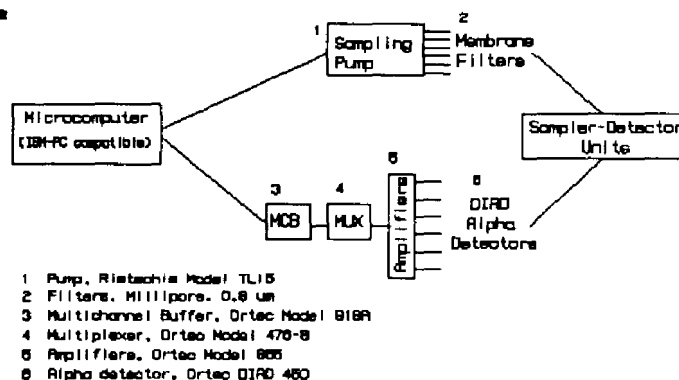


Figure 2. Schematic representation of the various components of the measurement system.

The upper section of each sampler-detector unit incorporates an ORTEC Model DIAD II ruggedized, 450 mm² surface barrier alpha detector sealed into an aluminum block. The detector is positioned in the aluminum block, concentric with the filter in the lower aluminum block and detects the alpha particles emitted by the ²¹⁸Po and ²¹⁴Po atoms collected or formed on the filter. The signals from the alpha detectors are connected through amplifiers into an 8-segment multiplexer and routed to an personal computer-based multichannel analyzer.

Figure 2 is a schematic diagram of the various components of the measurement system. A dedicated microcomputer controls acquisition of the alpha spectra, operation of the sampling pump, sample time sequencing, and data analysis. A typical sequence utilized in sampling air with 1-20 Pci/l of radon involves a 15 min sampling interval during which the first alpha spectrum is acquired followed by a 20 min delay period and a 40 min second alpha counting period prior to data analysis. The next sample is then begun following a delay period of between 15 min to 100 min to permit further decay of the ²¹⁴Pb and ²¹⁴Bi. The delay period duration is chosen based on sensitivity constraints imposed by the residual alpha counts remaining from the previous sample(s) since the filters are not changed between samples. This sequence of sampling, counting, and analysis permits automated, semi-continuous operation of the system with a frequency of between 1.5 to 3 hours.

The alpha counts from ²¹⁸Po and ²¹⁴Po detected by each alpha detector in the two counting intervals are used to calculate of the radon decay product concentrations penetrating into each unit (14). The observed concentrations of ²¹⁸Po, ²¹⁴Pb and ²¹⁴Bi are used to reconstruct the corresponding activity-weighted size distributions using the Expectation-Maximization (7) or Twomey (15) algorithms. The penetration characteristics of the 5 stages with screens are calculated using the Cheng-Yeh penetration theory since the wire screen parameters used in these samplers are identical to those of Yeh *et al.* (16). This theory has been verified experimentally in the size range $d_p > 4$ nm (2,3,12). The theory was also recently assessed to be accurate in the cluster size range for 30 and 145 in⁻¹ mesh screens using a ²¹⁸Po cluster aerosol, $D_{avg}=0.078\pm0.003$ cm²/sec (10).

The determination of optimum sampler-detector design and operating parameters (sampler

diameter, slit width, detector-filter distance and sampling flow rate) were determined by experimental testing of a prototype sampler-detector unit in a 2.43 m³ radon-aerosol chamber and theoretical studies that are described by Ramamurthi (8) and Ramamurthi *et al.* (10). Table I presents details of 6 optimized sampler-detector units.

Table I. Design and operating parameters for the optimized measurement system.

Unit	Sampler Slit Width (cm)	Sampler Diameter (cm)	Wire Screen Mesh x Turns	d _p (50%) (0.5-500 nm range) (nm)
1	0.5	5.3	-	-
2	0.5	5.3	145	1.0
3	0.5	5.3	145 x 3	3.5
4	0.5	5.3	400 x 12	13.5
5	1.0	12.5	635 x 7	40.0
6	1.0	12.5	635 x 20	98.0

Sampling flow rate = 15 lpm (each unit)

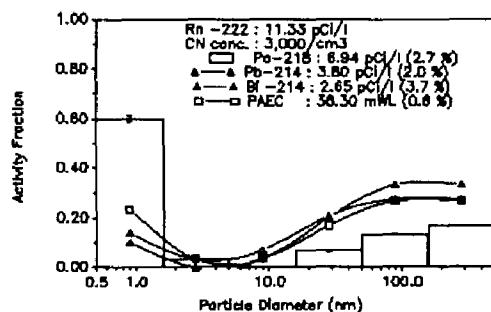
Detector-Filter separation ~ 0.8 cm (all units)

The number of stages (six) and stage progression shown in Table I was based on the conclusions of the simulation study. The study also yielded concepts regarding the optimum size resolution that could be obtained from the measurement system. The number and width of the size intervals used in the reconstruction process was dictated by considerations of size distribution accuracy and stability. An optimum number six inferred size intervals in geometric progression within the 0.5-500 nm size interval were thus selected. This progression of size intervals maximizes the differences in penetrability through the various stages insuring solution accuracy and stability while yielding sufficient size resolution in the inferred activity distribution.

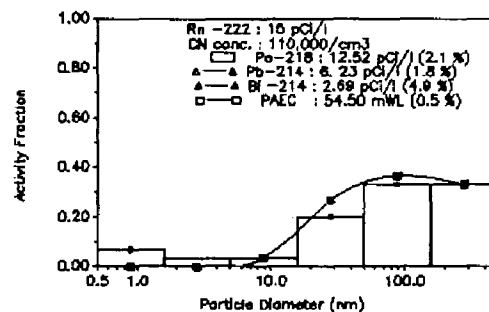
FIELD MEASUREMENTS

Measurements were made in a one-story residence with living room, dining room, kitchen, two bedrooms, a study room, two bathrooms, and basement in the Princeton, N.J. area. Activity size distributions were measured in the living room and the bedroom over two week period (1/16-1/31/90). A total of about 10 measurement were made in the living room and more than one hundred measurements in the bedroom with different types of particle generation. Aerosols were generated from candle burning, cigarette smoking, vacuuming (electric motor), cooking, and opening door from normal activities in the domestic environments. The particle concentrations were measured by using a Gardner manual condensation nucleus counter. The concentration and size distribution of radon progeny were determined by a semi-continuous graded screen array system. A sequence (0-15, 0-15, 15-35, 35-75) with 75 minute sampling was chosen because the radon concentration was in the range of 5 pCi/l - 50 pCi/l.

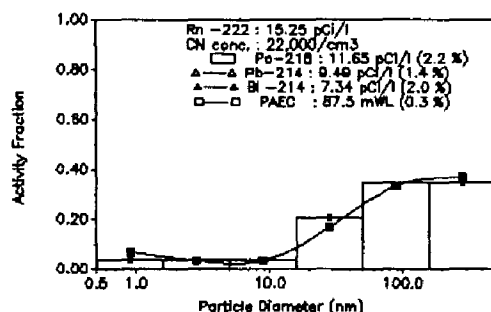
The influence of cigarette smoking (20 minutes) on the radon progeny size distributions in a closed bedroom are shown in Figure 3. The measurements were made 5 min after lighting the cigarette (5-20 min), 80 min later (80-95 min), and 155 min later (155-170 min). The fraction of ²¹⁸Po in 0.9 nm size range changed from 60% to 8%. The fraction of ²¹⁴Pb and ²¹⁴Bi in 0.9 nm size range was about 10% and becomes essentially zero. The fraction of three distributions in 1.5-15 nm size range stayed the same. There is a large increase (from 40% to 80%) of ²¹⁸Po in the "attached" mode (50-500 nm size range) with insignificant changes (from 35% to 40%) in ²¹⁴Pb and ²¹⁴Bi fractions in this mode.



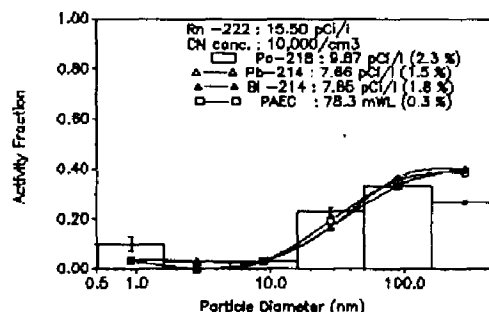
A: Background Size Distributions.



B: During the active smoking period.



C: 80 minutes later.



D: 155 minutes later.

Figure 3. Activity size distributions in a bedroom before, during, and after smoking a cigarette.

The influence of cooking on the radon progeny size distributions with an open bedroom door is shown in Figure 4. A steak was pan fried for 20 minutes (0-20 min) using a gas stove burner in the kitchen. The measurements were made 5 min later (5-20 min), 80 min later (80-95 min), and 155 min later (155-170 min). The fraction of ²¹⁸Po in 0.9 nm size range changed from 60% to 15%. The fraction of ²¹⁴Pb and ²¹⁴Bi in 0.9 nm size range changed from 15% to 10%. There is a very low fraction of activity in 1.5-15 nm size range for background and it increases to 10% because of cooking. A large increase (from 35% to 70%) of ²¹⁸Po is observed in the "attached" mode peaked in 50-500 nm size range with only small changes (from 40% to 50%) in ²¹⁴Pb and ²¹⁴Bi distributions.

Because of the large amount of particle generated by normal activities in the domestic environment, the working level will increase for a period of time while the "unattached" fraction will decrease. The particles generated from cigarette smoke and cooking dramatically shifted almost all of radon progeny to "attached" fraction and remained for a long period of time. The particles produced from candle burning and vacuuming were much smaller with the average attachment diameter around 15 nm. The candle and vacuuming particles did decrease the "unattached" fraction, but returned to the original background distributions about 150 minute later.

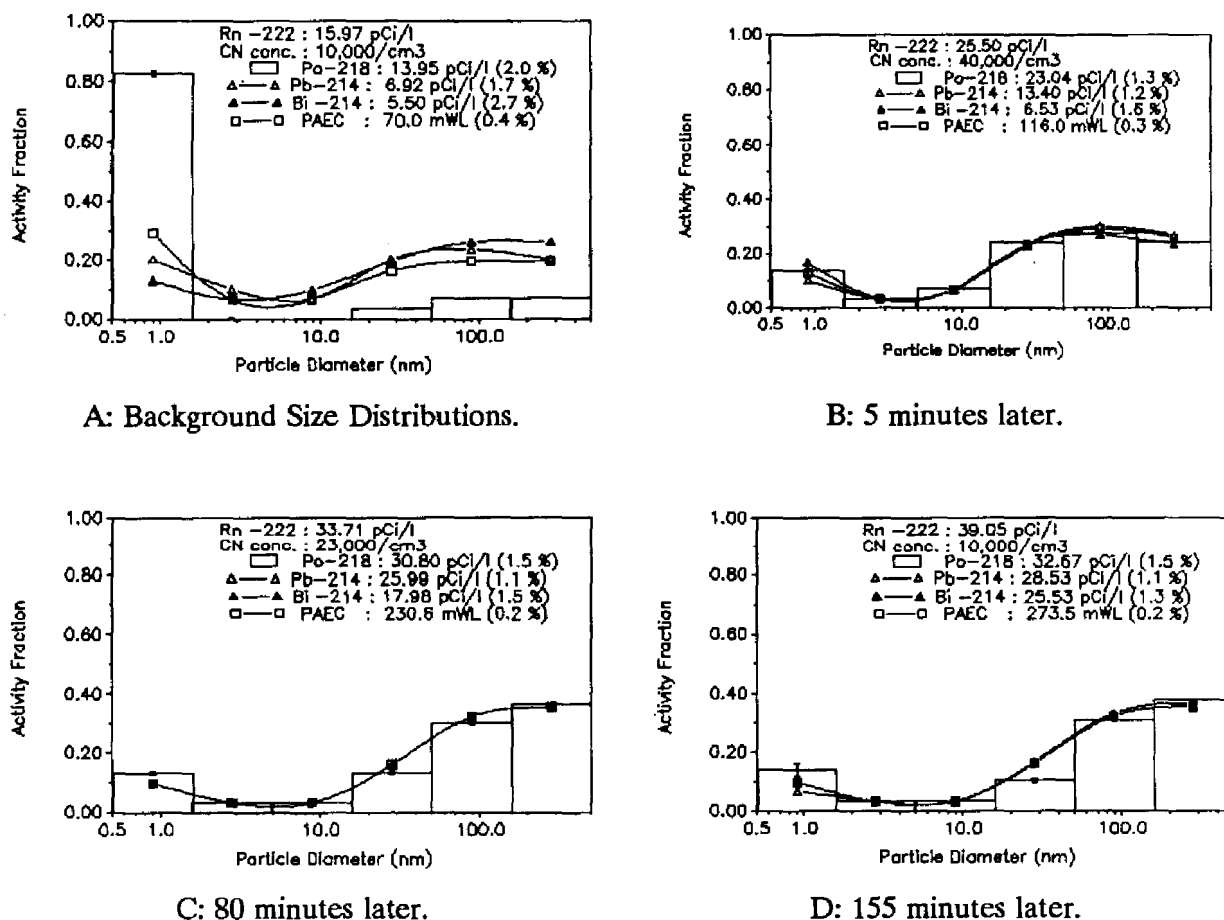


Figure 4. Activity size distributions measured in a bedroom during and after cooking in the kitchen.

SUMMARY

A measurement system has been developed for the purpose of characterizing indoor radon decay product radioactivity on an automated, semi-continuous basis. The system was designed and calibrated for sampling both the ultrafine cluster and attached modes of radioactivity present in indoor air, with the optimized design based on the results of both experimental and numerical simulation studies. The measurement system is capable of monitoring changes in activity concentrations and size distributions as a function of time and indoor events. Further measurements with the system should permit an improved estimation of the health hazards from radon decay products in indoor air.

ACKNOWLEDGMENTS

This work was supported by the U.S. Department of Energy under contract DE-FG02-89ER60876, and the New Jersey Department of Environmental Protection under contract J89-62. We would also like to gratefully acknowledge the assistance of Rian Strydom and Chih-Shan Li in the experimental work, as well as the collaboration of K. Gadsby, A. Cavallo, and R. Socolow of Princeton University in the field experiments.

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THE ATMOSPHERIC STABILITY OF POLYBROMINATED DIBENZO-p-DIOXINS AND DIBENZOFURANS

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ABSTRACT

Polybrominated dibenzo-p-dioxins (PBDDs) and polybrominated dibenzofurans are generated during the combustion of brominated organics such as polybrominated diphenyl ethers (PBDPEs) which are used as flame retardants in plastics, carpets and other materials (Buser 1986). Due to increasing use of PBDPEs, atmospheric emissions of PBDDs and PBDFs are likely to increase in the future. Regulating emissions of these compounds requires information on their atmospheric stability because biological exposure and uptake occurs via atmospheric transport and depositional processes. Laboratory experiments indicate that PBDDs and PBDFs rapidly photodegrade in solution and also degrade when sorbed on quartz surfaces. Unknown are the rates of PBDD and PBDF photodegradation under realistic outdoor conditions. In this study, we introduced emissions from the combustion of polyurethane foam containing PBDPEs into 25 m³ outdoor Teflon film chambers. Concentrations of tetra- and pentabrominated dibenzo-p-dioxins and dibenzofurans were monitored over time by collecting and analyzing filter and adsorbent samples. The results show that PBDDs and PBDFs are stable on soot particles over periods of hours and suggest that photochemical production of PBDFs and PBDDs from residual PBDPEs may occur.

INTRODUCTION

As incineration is becoming a more important form of disposal of wastes an assessment of risks associated with toxic organic emissions becomes vital. Polychlorinated dibenzo-p-dioxins have been a major focus of scientific investigation and public concern due to the toxicity of tetrachlorinated dibenzo-p-dioxin (TCDD) and tetrachlorinated dibenzofuran (TCDF) in guinea pigs ($LD_{50}=0.6\mu\text{g/kg}$ and $5-10\mu\text{g/kg}$, respectively, Poland and Glover, 1977). Polybrominated dibenzo-p-dioxins and dibenzofurans (PBDDs and PBDFs) are structurally similar compounds which are potentially either as or more toxic than their chlorinated analogs (Mason, 1987).

The combustion or photodegradation of polybrominated diphenyl ethers (PBDPEs) produces PBDDs and PBDFs. Yields of 19% were

observed for the thermolysis of pentabrominated diphenyl ether sorbed on quartz surfaces at 630C and 0.5-1% at 530C (Buser, 1986). Photodegradation of decabrominated diphenyl ether in hexane has been shown to produce PBDFs with a 10-20% yield by UV or sunlight irradiation (Watanabe and Tatsukawa, 1987).

In 1988, polybrominated diphenyl ethers were produced at a rate of 75 million pounds with production expected to increase at a rate of ten to fifteen percent per year (Mazek, 1988). Due to increasing production and use of incineration, emissions of PBDDs and PBDFs are likely to increase in the future. The atmospheric behavior of these compounds affects biological exposure through transport and deposition processes. Thus in order to understand the potential impact of these emissions, information on the atmospheric stability of PBDDs and PBDFs is needed.

A paucity of data exists on the decay of PBDDs and PBDFs once formed under realistic atmospheric conditions. In laboratory experiments, PBDDs and PBDFs readily degrade by debromination with half lives on the order of minutes in solution and hours on surfaces (Buser, 1988). Work has previously been done to evaluate the atmospheric stability of polycyclic aromatic hydrocarbons on realistic soot particle surfaces (Kamens, 1987). This work helps form the methodological basis for this research discussed whose overall objective is to study the stability of PBDDs and PBDFs on incinerator soot particles under realistic outdoor conditions.

METHODOLOGY

Polybrominated dibenzo-p-dioxins and furans were produced in a small scale incinerator from known precursors (industrial grade pentabrominated diphenyl ether as 8.5% w/w component of polyurethane foam), introduced to a 25 m³ outdoor teflon chamber and allowed to age within this captured air parcel (see Figure 1). During the aging period, samples were collected on 47 mm T60 420 teflon impregnated glass fiber filters followed by a 4" x 1.5" polyurethane foam trap (see Figure 1). Additional atmospheric variables monitored include ozone concentrations, nitrogen oxide concentrations, total solar radiation, temperature and particle size. These results are summarized in Table 1. In the laboratory, ¹³C₁₂ labeled PBDDs and PBDFs were added as internal standards and the samples were soxhlet extracted in toluene. The extracts were then passed through a series of three gravity columns; acidic silica gel, florisil and carbon/celite to separate PBDDs and PBDFs from other components in the extract. The resulting extracts were analyzed by GC/MS by selective-ion-monitoring at a resolving power = 10,000. The results for the tetra- and penta- brominated dibenzo-p-dioxins (TBDDs and PeBDDs) as well as tetra, penta and hexa dibenzofuran (TBDFs, PeBDFs and HxBDFs) are reported on a congener basis.

RESULTS AND DISCUSSION

The results of initial samples for two experiments conducted on Dec. 20, 1989 and March 14, 1990 are reported. Comparison of these results provides a means of assessing the starting points for the chamber aging experiments. Concentrations varied by orders of magnitude for the congener classes monitored following the order TBDF > TBDD, PeBDF > PBDD > HxBDF (Figure 2). This is expected since the formation of PBDFs from PBDPEs is an intramolecular process while the formation of PBDDs from PBDPEs is an intermolecular process. The preponderance of lower brominated species can be explained by the primary abundance of pentabrominated diphenyl ether in the flame retardant material and simultaneous debromination reactions occurring during thermolysis (Buser, 1986). Comparison of the initial vapor and particulate samples shows that in each case the particulate concentration exceeds the vapor phase concentration by at least two orders of magnitude (Figure 3).

Samples were obtained over the course of a two hour period in each of these experiments (Figure 4). Concentrations of PeBDD remained steady at approximately 0.6 ng/mg on Dec 20. PeBDD concentrations on March 14 began at 1.8 ng/mg and remained steady or perhaps exhibited a slight decline over time. Similarly PeBDF held steady at approximately 13 ng/mg during the Dec 20, 1989 experiment and held steady or slightly decreased from a level of 68 ng/mg on March 14. Similarly the March 14 experiment showed HxBDF to be stable or slowly decaying from a concentration of 540 pg/mg. These results suggest degradation half lives on the order of many hours. This implies that Buser's quartz surface experiments are a better predictor of rates on realistic particles than his solution experiments.

Results from the other congener classes were more surprising. TBDF concentrations (3-6 ug/mg) appeared to slightly increase midway through the sampling period and then decline. This cannot be explained by the debromination of PeBDF due to the differences in concentrations between TBDF (ug/mg) vs. PeBDF (ng/mg) but may be evidence for photolysis of PBDPEs that survived the combustion process in a reaction similar to that observed by Watanabe and Tatsukawa (1987). TBDD seemed to be steady or decay from a concentration of 140 ng/mg on Dec 20 and increase on March 14 from 9.2 to 12.9 ng/mg. Further experiments are needed to determine if these trends are due to analytical variability or photolytic production. Some rationale exists for why photolytic production may be occurring in the tetra congener classes and not in others. Watanabe and Tatsukawa (1987) found the reaction to occur with simultaneous debromination and our starting material was the pentabromo diphenyl ether primarily. On March 14 the initial concentration of TBDD was relatively low perhaps allowing formation processes to outweigh

degradation processes for a time. It is important to note that Watanabe and Tatsukawa (1987) observed photolytic formation for PBDF and not PBDD. However, it is possible that the availability of oxygen donating species needed for the formation of dioxins is less in hexane solution than on soot particle surfaces under atmospheric conditions.

Aerosol size distributions monitored from the December 20 experiment revealed that though the total number of particles in the chamber decreased over time (probably due to air infiltration, removal of sample and diffusion to the walls) the overall size distribution remained fairly constant (Figure 5).

CONCLUSIONS

Additional work is needed to deconvolute rates for the processes that seem to be occurring; degradation through debromination of PBDDs and PBDFs and formation of TBDDs and TBDFs from PBDPEs. However several conclusions can be reached from this initial work. At 650C-675C substantial quantities of PBDD and PBDF are produced from the combustion of small amounts (0.59 to 0.7 g) of polyurethane foam containing polybrominated diphenyl ethers. Particulate phase concentrations of PBDDs and PBDFs seem to remain relatively steady over periods of hours under realistic atmospheric conditions. The data suggest that a photolytic production of TBDDs and TBDFs from PBDPEs may be occurring. In addition, procedures and protocols developed can be applied to study the atmospheric stability of other toxic organics emitted during incineration.

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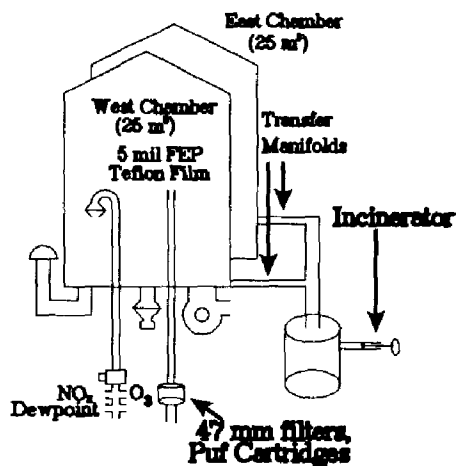


Figure 1: Schematic diagram of experimental apparatus.

Table 1: Comparison of conditions for chamber aging experiments.

	Dec. 20 1989	M ₁
CHAMBER TEMPERATURE (°C)	5 to -2	20
DEW POINT (°C)	-5.0	1
[NO] (ppm)	0.040	0.1
[NO ₂] (ppm)	0.036	0.1
[O ₃] (ppm)	0.019	.2
INCINERATOR TEMPERATURE (°C)	660	6
TOTAL SOLAR RADIATION (Cal cm ⁻² min ⁻¹)	0.7 to 0.05	0. to 1

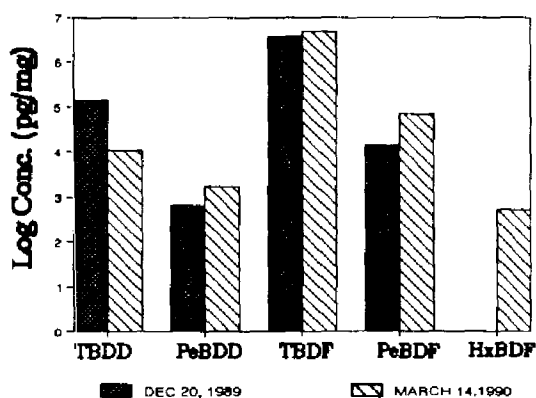


Figure 2: Comparison of the first filter sample in each chamber aging experiment.

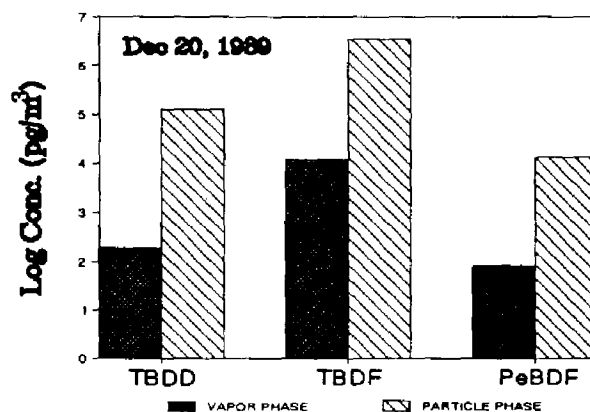


Figure 3: Comparison of vapor and particle phase concentrations for the initial sample in the Dec. 20, 1989 experiment.

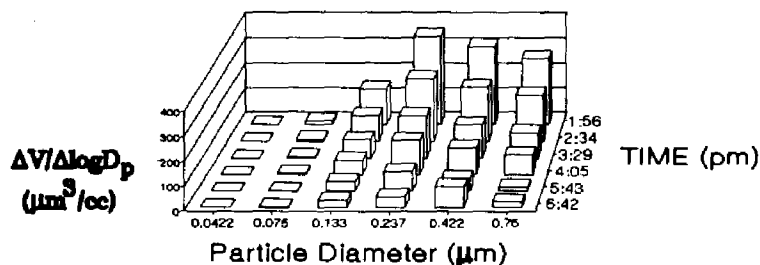


Figure 5: Volume size distribution of particles in chamber during the course of the Dec. 20, 1989 experiment.

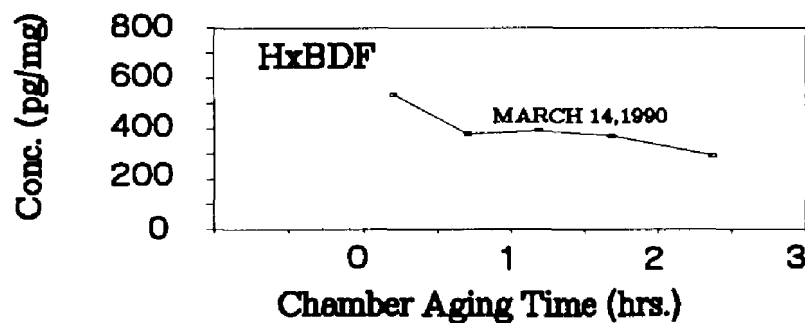
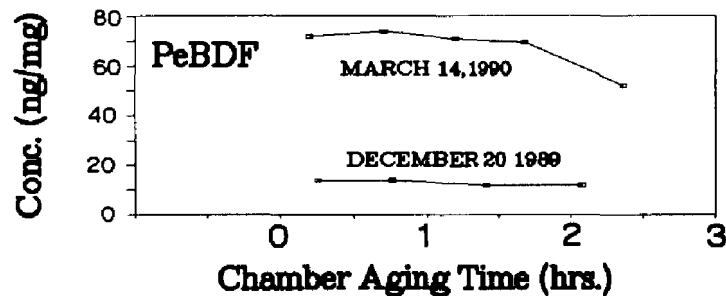
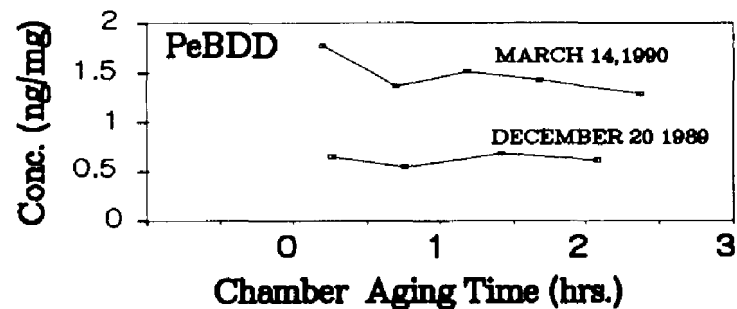
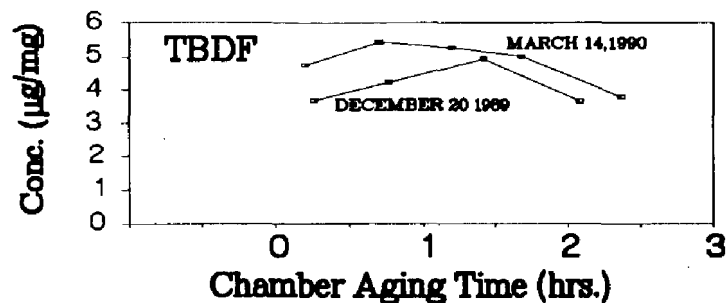
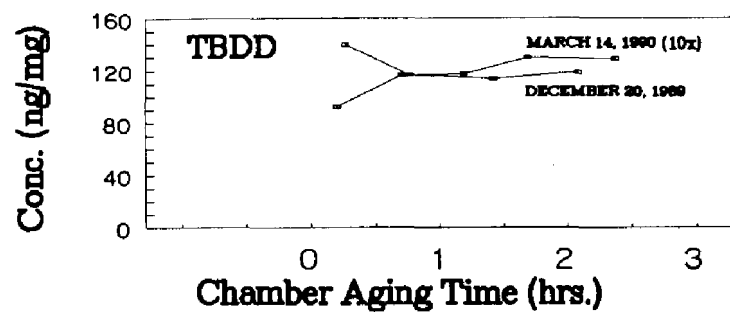


Figure 4: Concentrations of PBDDs and PBDFs during chamber aging period.

OCCURRENCE AND VAPOR PARTICLE PARTITIONING OF HEAVY ORGANIC COMPOUNDS IN BRAZZAVILLE, CONGO

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INTRODUCTION

Organochlorine (OC) insecticides are used in several tropical and subtropical countries for malaria control and for commercial agriculture. Whereas DDT has been banned in North America and Europe, Third World countries still use DDT in the war against malaria and sleeping sickness and in agriculture (1-3). In India and Central America re-emergence of malaria has accompanied the rapid spread of mosquito resistance caused by elevated application of DDT during the late 1960s and 1970s (4). Dispersal of pesticides through the atmosphere is responsible for environmental contamination on a regional and global scale (5-8). Reports of high levels of DDT in the Indian troposphere have shown that India has become a point source (9-10). DDT consumption in Africa in the period between 1980-1989 was 1294 tonnes (11). In Zimbabwe, wildlife has been contaminated with the DDT used in the irradiation of the tse-tse fly (3). High levels of DDT in plants from the west coast of Africa is indicative of local use (12). DDT volatilization from tropical soils has been reported (13). DDT residence time in soils under tropical conditions is relatively short because of volatilization which is considered to be the most important pathway of dissipation in atmosphere (14-15). Is Africa another point source of DDT and other OC insecticides? To the best of our knowledge no information exists on atmospheric transport of pesticides in Africa. This work was carried out to determine the types and levels of airborne pesticides, polychlorobiphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) in Brazzaville, Congo, and to assess the distribution of these compounds between the particle and gas phases in atmosphere.

EXPERIMENTAL

Air samples ($331-680 \text{ m}^3$) were collected during August-September, 1989 at the top of the American Cultural Center in Brazzaville, Congo (4.14°S , 15.14°E) using a high volume sampler containing two glass fiber filters and two polyurethane foam plugs. The average sampling temperature was 25°C . The average TSP was $56 \mu\text{g m}^{-3}$. Samples were shipped to the University of South Carolina where they were extracted and analysed by capillary GC with electron capture detection (OCs) and GC-MS with selected ion monitoring (PAHs). Collection and analytical methods are described elsewhere (16-17).

RESULTS AND DISCUSSION

a) Organochlorine Pesticides

The mean concentrations (ng m^{-3}) of DDT-related compounds, hexachlorocyclohexanes (HCHs), and chlordanes are shown in Table 1 and are compared with those found from various locations of the world in Table 2. Total DDT in Brazzaville (3.0 ng m^{-3}) ranged between levels reported in Porto Novo and New Delhi (South-India) where DDT is still used, and was 30-100 times higher than the levels found in European and North American countries where DDT is not used. In Brazzaville, p,p'-DDT was the prevalent isomer followed by p,p'-DDD, o,p'-DDT and p,p'-DDE.

Africa consumed 5213 tonnes of HCH products from 1980 to 1989 (11).

The levels of total HCH (0.39 ng m^{-3}) in Brazzaville were comparable to those reported from European and North-American cities and 40 to 3000 times smaller than those reported from India (Table 2). With a mean concentration of 0.35 ng m^{-3} , γ -HCH was the predominant isomer. HCH products are used in many countries for antimalarial and agricultural purposes. In central Europe where pure lindane (99.5% γ -HCH) is used, γ -HCH concentrations exceed those of α -HCH (18-20). In India technical HCH (70% α -HCH, 14% γ -HCH, 9% β -HCH and 7% δ -HCH) is largely used and in most cases α -HCH > γ -HCH (9,10). In Brazzaville, ratios of γ -HCH to α -HCH ranged between 6.8 to 12.7 with an average of 9.3. This high γ/α ratio can only be due to the use of γ -HCH and not technical HCH.

Typical Southern Hemisphere levels of chlordane (ng m^{-3}) have been reported (8,21). Eastern Indian Ocean: 0.02, western Australia: 0.027, Reunion: 0.013-0.027. In Brazzaville the mean concentration of chlordane (cis- + trans-chlordane + trans-nonachlor = 0.04 ng m^{-3}) was comparable to the levels in the atmosphere of the open Southern Hemisphere oceans, and 15 - 43 times smaller than in Columbia, SC and Hyogo, Japan. Major chlordane use in the U.S.A and Japan has been for termite control and has led to fairly high levels in ambient air. The fact that chlordane concentrations in Brazzaville are similar to open-ocean concentrations suggests that little or no local use occurs.

b) PCBs and PAHs

The mean PCB concentration was 0.60 ng m^{-3} . This concentration is slightly lower than observed in U.S. cities and closer to that reported from Hyogo, Japan. Figure 1 shows the distribution of PCB congeners in the air of Brazzaville. The mean concentrations of PAHs are also shown in Table 1. As with PCBs, PAHs with higher vapor pressures predominated. For example, phenanthrene represented more than 45% of the total PAH. PAH levels in Brazzaville were almost six times lower than those reported from Osaka, Japan and comparable to those found in U.S. cities (Table 2).

Table 1. Organochlorine Pesticides, Σ PCB and PAH in Brazzaville Air

Pesticides and Σ PCB		PAH	
Compound	ng/m^3	Compound	ng/m^3
p,p'-DDT	1.26	PH	21.60
o,p'-DDT	0.59	MePH	5.32
p,p'-DDD	0.73	AN	1.94
p,p'-DDE	0.45	FLA	5.36
γ -HCH	0.35	PY	5.84
α -HCH	0.04	BaA	0.48
trans-chlordane	0.01	CHRY	1.10
cis-chlordane	0.02	BbF	0.76
trans-nonachlor	0.01	BkF	0.63
Σ PCB	0.60	BeP	0.44
		BaP	0.25
		BghiP	0.85

PH = Phenanthrene

MePH = Methylphenanthrene

AN = Anthracene

FLA = Fluoranthene

PY = Pyrene

BaA = Benz(a)anthracene

CHRY = Chrysene

B(b)F = Benzo(b)Fluoranthene

B(k)F = Benzo(k)Fluoranthene

B(e)P = Benzo(e)pyrene

B(a)P = Benzo(a)pyrene

B(ghi)P = Benzo(ghi)perylene

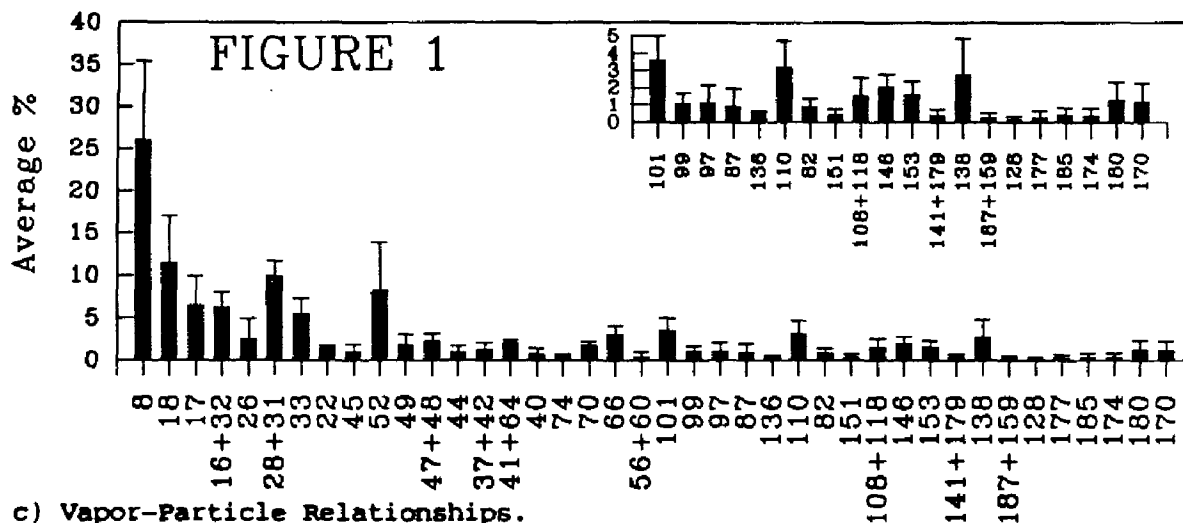
Table 2. Concentrations Pesticides, PCBs and PAHs from Different Locations, ng/m³

Locations and Survey Year	ΣDDT	ΣHCH	Chlordane	ΣPCB	PH+AN+FLA+PY	BeP+BaP	References
Brazzaville, Congo 1989	3.03 ^a	0.39	0.04	0.60	35	0.70	This work
Delhi, India 1980-1982	46-73 ^a	160-930					9
Porto-Novo 1987-1989	0.28 ^a	15					10
Columbia, SC (USA) 1977-1980	0.14 ^b	1.10	0.60	30	54	0.50 ^g	17, 27
Denver, CO (USA) 1980	0.02 ^c	0.30	0.07	2.2			17
1985	0.03 ^a		0.06	2.0	79	1.7 ^g	26
Portland, OR (USA) 1984-85	0.08 ^c	0.34			46	2.4	29, 22
Delft, Netherlands 1980	0.12 ^a	0.61		0.96	<8.5-11.5	<0.3-6	19
Paris, France 1986-87	<0.05-0.22 ^c	1.6		5.44			20
Ulm, West Germany 1986	0.025 ^c	3.0					18
Southern Sweden 1983-85	0.007	0.49	0.01	0.29			17
Hyogo, Japan 1988			1.7	0.45			28
Osaka, Japan 1982					185	11.2	30
Réunion, Southern Indian Ocean 1986	0.03 ^c	0.41	0.015	0.03 ^f			8

a = pp'-DDT+op'-DDT+p,p'-DDD+pp'-DDE
g = only BaP

b = p,p'-DDT+p,p'-DDE
f = congener (28-180)

c = p,p'-DDE



c) Vapor-Particle Relationships.

To assess the removal mechanisms, reactivity and health effects due to inhalation of organic compounds in the atmosphere, the study of the vapor-to-particle partitioning is required (22). Many researchers have shown that the relationship between the apparent vapor-to-particle ratio and the liquid vapor pressure of the organic compounds (P_L^O) at a given temperature is:

$$\text{Log } (A/F)/\text{TSP} = m\text{Log}P_L^O + b \quad (1).$$

TSP is the particle concentration ($\mu\text{g m}^{-3}$). A and F are adsorbent and filter-retained concentrations of organic compounds (ng m^{-3}). These were calculated from quantities found on the two filters and PUF plugs using relationships given by Ligocki and Pankow (22). Average percentages of particulate OCs and PAHs were: p,p'-DDT = 5, o,p'-DDT + p,p'-DDD = 3, p,p'-DDE = 1, BeP + BbF + BkF > 80, chrysene = 20, fluoranthene = 1.2, phenanthrene = 0.40. Plots of (1) for OCs and PAHs are shown in Figures 2 and 3. Values of P_L^O were from the literature (23,24). Slopes, intercepts, and R^2 values were: OCs: $m = 0.74$, $b = 5.76$, $R^2 = 0.97$. PAHs: $m = 0.85$, $b = 5.29$, $R^2 = 0.96$.

Figure 4 shows a comparison between the fraction of particle-associated organic compounds as described by Junge-Pankow (J-P) model and by Brazzaville data. The J-P model is:

$$\phi = cS_T / P_L^O + cS_T \quad (2)$$

Where $\zeta = 17.3 \text{ pa-cm}$ (22); S_T = Particle surface area per volume of air (cm^2/cm^3). The curves for Brazzaville OCs and PAHs were calculated from:

$$\phi = 1/[1+(A/F)] \quad (3).$$

The field data for PAHs were very close to J-P curve. The differences between PAHs and OCs suggest different strengths of adsorption. This was seen in a comparison of PAH data from Tokyo and OC data from Columbia and Stockholm (25) but not seen for PAHs and OCs in Denver (26). However the fractions of OCs on particles in Brazzaville were very small and the liquid vapor pressure range of OCs examined was much less than for the PAHs.

ACKNOWLEDGEMENTS

Support was provided by the International Agency for International Development and the National Science Foundation. We are grateful to the authorities of the American Cultural Center in Brazzaville for allowing us to use their building.

FIGURE 2

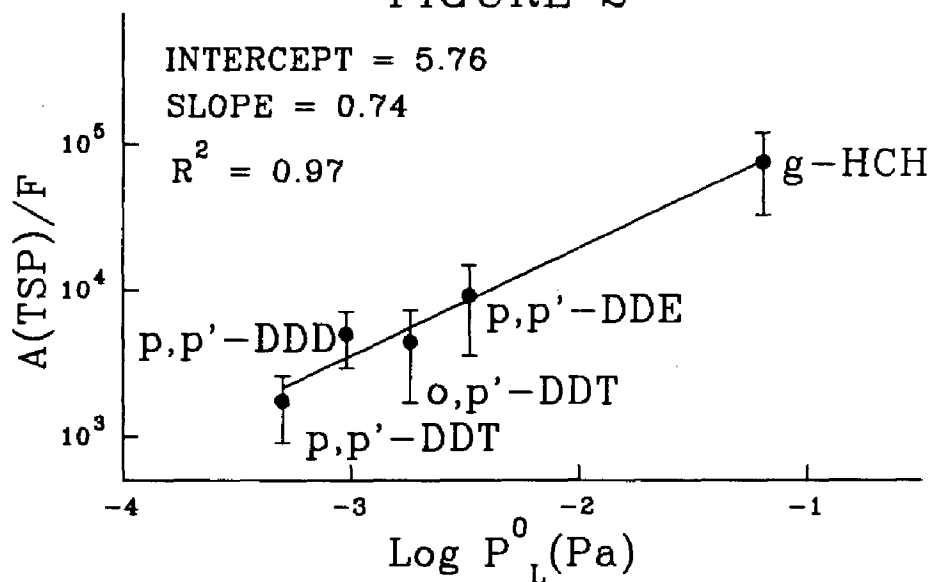


FIGURE 3

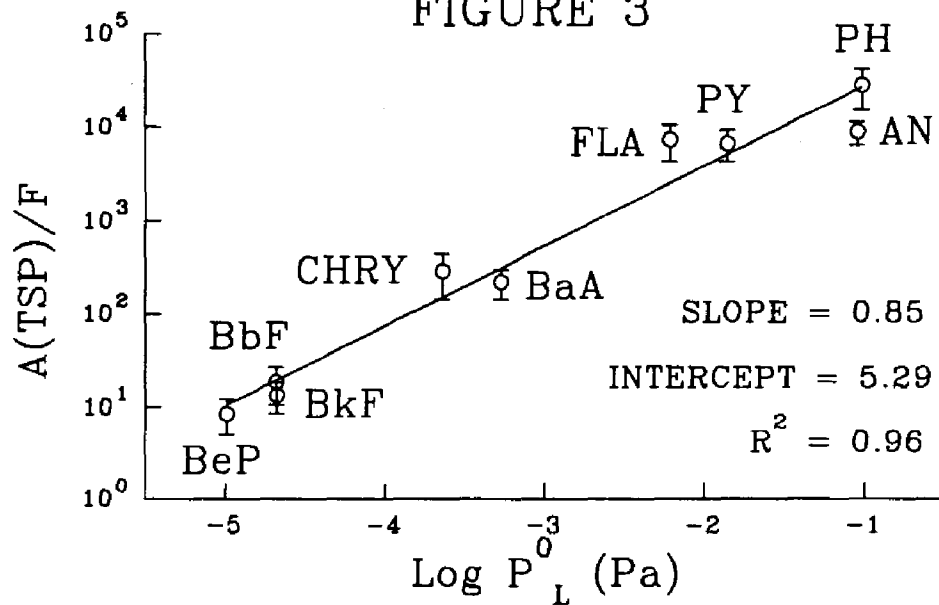
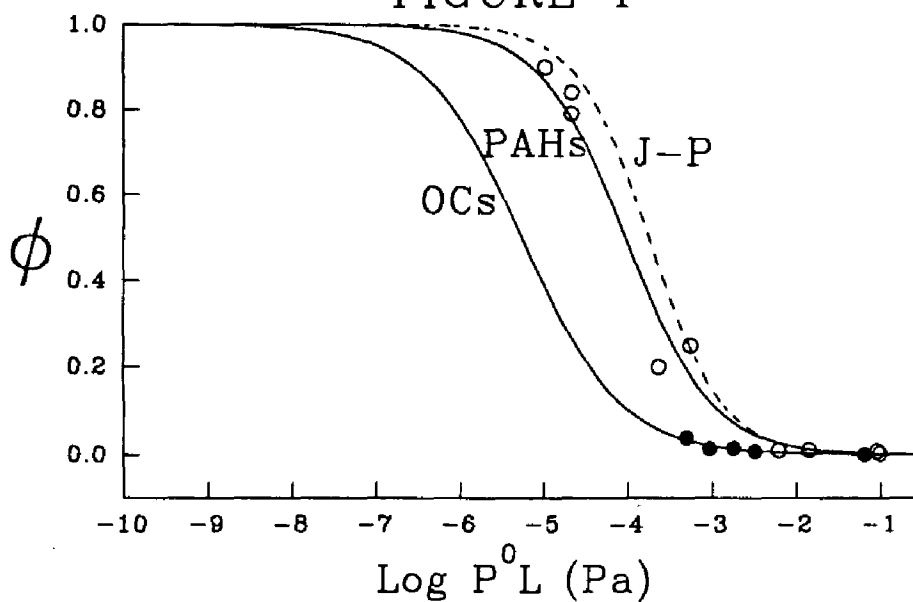


FIGURE 4



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**Heterogeneous Reaction of Nitrogen Oxides
on Sea Salt and Mineral Particles -
A Single Particle Approach**

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Heterogeneous reactions of NO_2 and HNO_3 at sub ppm levels with sea salt and mineral particles were investigated. Experiments were conducted in a static reaction chamber made of Teflon, where particles deposited on filters and on electron microscope grids were exposed to NO_2 or HNO_3 under controlled conditions. Nitrates formed on the particle loaded filters were determined by bulk analysis. In parallel, sea salt and mineral particles were observed in an electron microscope to detect the presence of nitrate on the surfaces of each individual particle. Microspot techniques were applied for the latter.

Under the present experimental conditions the formation of nitrates on sea salt particles was in the range of 0.1 to 3.3 mg $\text{NO}_3^-/\text{g NaCl}$. Slightly higher values were obtained for mineral particles: 0.2 to 4.7 mg NO_3^-/g aerosol ($[\text{NO}_2]=0.18$ ppm and 0.54 ppm; $[\text{HNO}_3]=0.04$ ppm; exposure time 1 to 8 days; relative humidity =70%).

Application of electron microscopy and specific microspot techniques provided direct evidence for the heterogeneous reaction of sea salt and mineral particles with NO_2 and HNO_3 to form a layer of nitrate on the particle surfaces. Forty to 50% of the soil and almost all sea salt particles that were exposed to NO_2 and HNO_3 form mixed nitrate particles.

Introduction

The presence of ammonium nitrate in the fine particle mode and nitrates associated with sodium or minerals in the coarse mode has been documented by several groups¹⁻⁵. The fine particles are formed through homogeneous gas phase, while the coarse mode is formed through the reaction of sea salt and mineral particles with nitrogen oxides. No direct evidence was provided. Other heterogeneous processes for nitrate formation involve reaction of gaseous nitric acid with sea salt particles⁶.

It is the purpose of this research to use electron microscopy techniques to study the reactions between sea salt or mineral particles and nitrogen oxides or nitric acid, and to provide direct evidence for the formation of nitrates on the surfaces of ambient particles.

Experimental

Laboratory studies of heterogeneous reactions between atmospheric particles and nitrogen oxides were carried out in a static Teflon chamber, under controlled conditions and no illumination. NaCl, CaCO₃, sand, soil, and sea salt particles were deposited on electron microscope grids, and on 47 mm Nuclepore and Teflon filters. The latter were used for bulk analysis. The particles were exposed to known concentrations of NO₂ (0.18 and 0.54 ppm) or HNO₃ (0.04 ppm) at 70% relative humidity (RH), using permeation tubes. Exposure varied from 1 to 8 days. Any formation of nitrate on loaded filters were determined by standard wet chemistry methods.

Electron microscope grids were investigated using microspot and electron microscopy techniques⁷. Bulk analysis allowed to quantify nitrate formation in terms of mg NO₃⁻/g aerosol, while microscopy provides direct evidence of such formation.

Results and Discussion

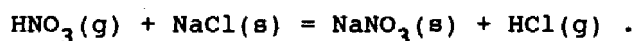
Bulk Analysis

In this study changes in relative humidity (40% to 85%) were found to have a negligible effect on nitrate formation. A 70% RH was therefore chosen for all experimental runs. Figure 1 is a plot of the nitrate formation for different aerosols exposed to 0.54 ppm and 0.18 ppm NO₂ from one to 7 days. The Figure indicates that exposure of particles to higher NO₂ concentrations results in higher nitrate capacities. Capacities (mg NO₃⁻/g aerosol) are defined as the maximum quantity of nitrates in mg formed on one gram of aerosol. Figure 2 shows nitrate formation versus time for exposure to 0.04 ppm HNO₃ at 70% RH. Nitrate capacities for sea salt (including NaCl) and minerals were around 3 and 3 to 5 mg NO₃⁻/g aerosol respectively.

Individual Particle Analysis

Particles collected on Nuclepore filters were observed in the microscope before and after they were exposed to NO₂ and HNO₃. No significant changes

in particle morphology were detected. The particles collected on electron microscope grids, after exposed to nitrogen oxides, were coated with a thin layer of nitron⁷ in order to detect the presence of nitrate formation on the particle surfaces. Forty five to fifty percent of the mineral particles reacted with either NO₂ or HNO₃ to form mixed nitrate-mineral particles. Figure 3 is a photomicrograph of a mineral particle that reacted to form nitrate on its surfaces. The mineral particle is surrounded by characteristic fibers, the result of nitrate reaction with the nitron film⁷; thus this micrograph provides direct evidence for the nitrate formation on the particle surface. Not all minerals had reacted to form nitrates. Particles that formed nitrate seem to be identical to those without any nitrate formation. Only that the later group had a larger size range. Almost all sea salt and NaCl particles reacted with the above gases as expected, following the well known equation :



In this case the reaction was not always on the surface but rather a reaction with the whole particle mass.

Acknowledgements

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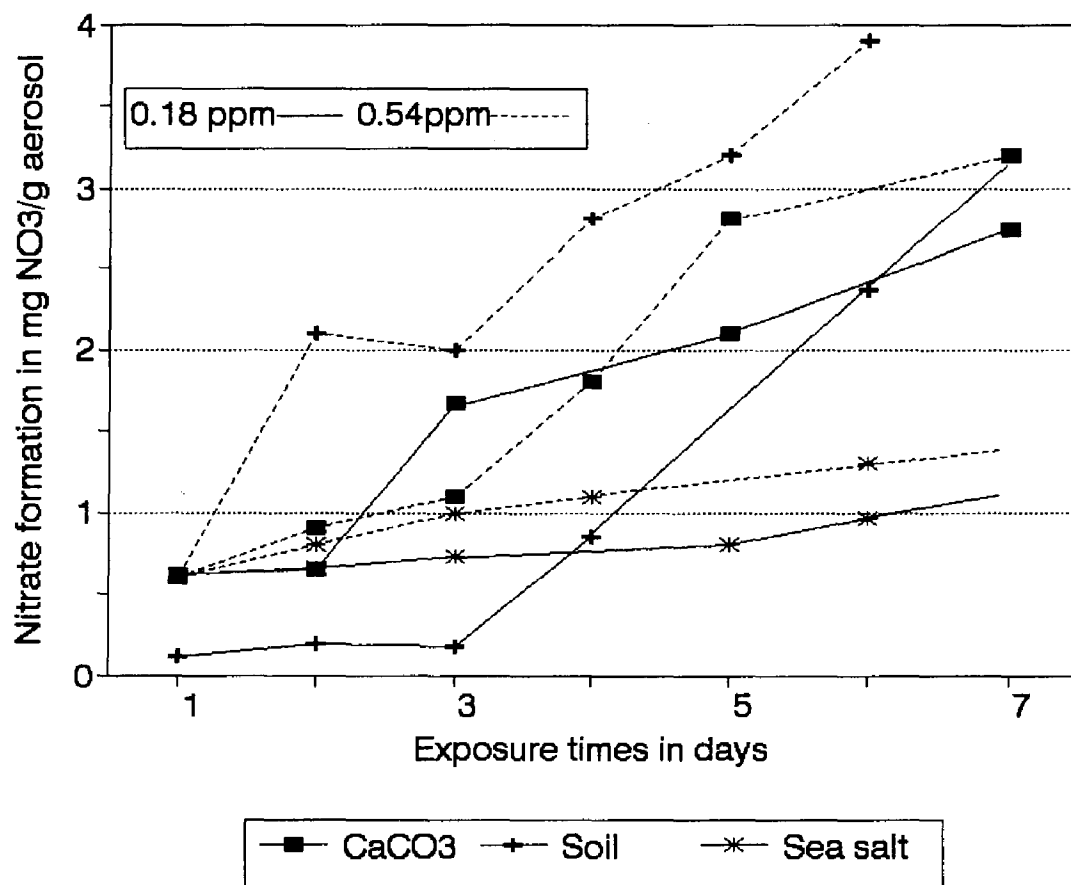


Figure 1. Formation of nitrate, in terms of mg nitrate per g of aerosol, on carbonate, soil and sea salt aerosol as a function of exposure time. NO₂ concentrations were 0.18 and 0.54 ppm.

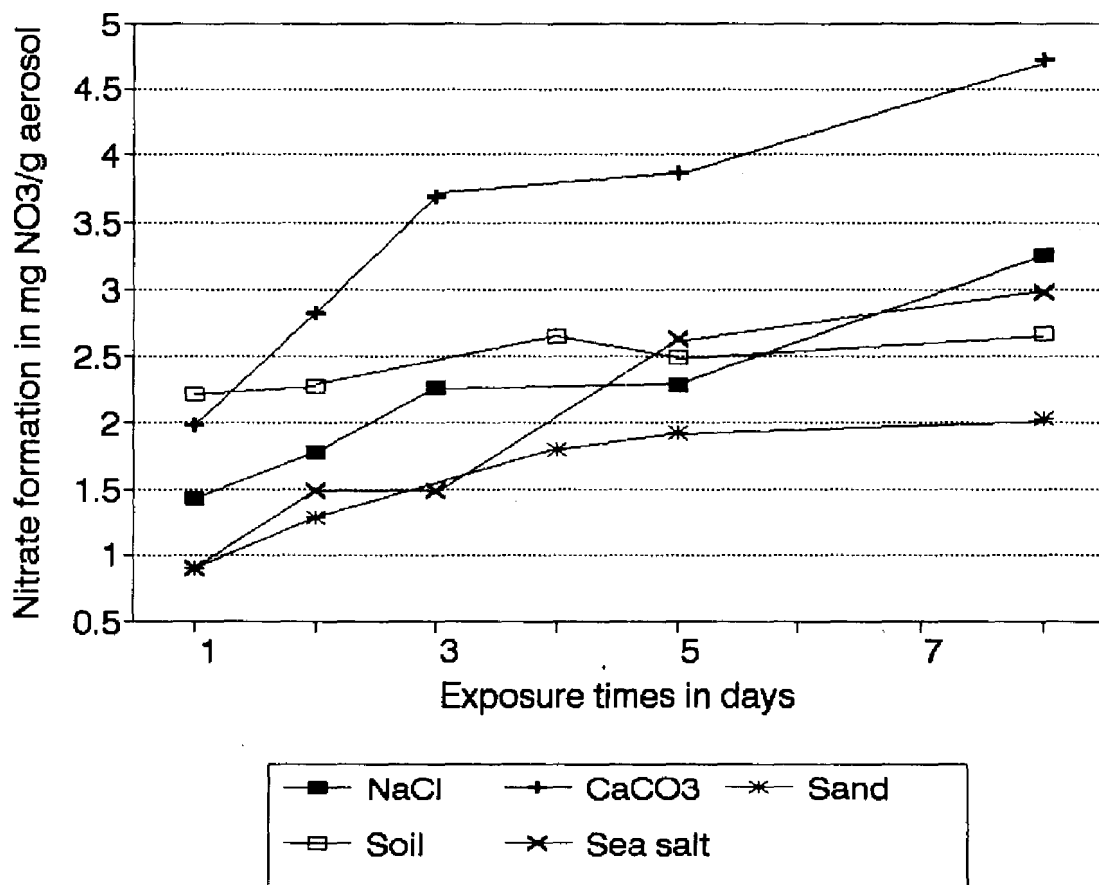


Figure 2. Formation of nitrate, in terms of mg nitrate per g of aerosol, on NaCl, carbonate, sand, soil and sea salt aerosol as a function of exposure time. HNO₃ concentration was 0.04 ppm.

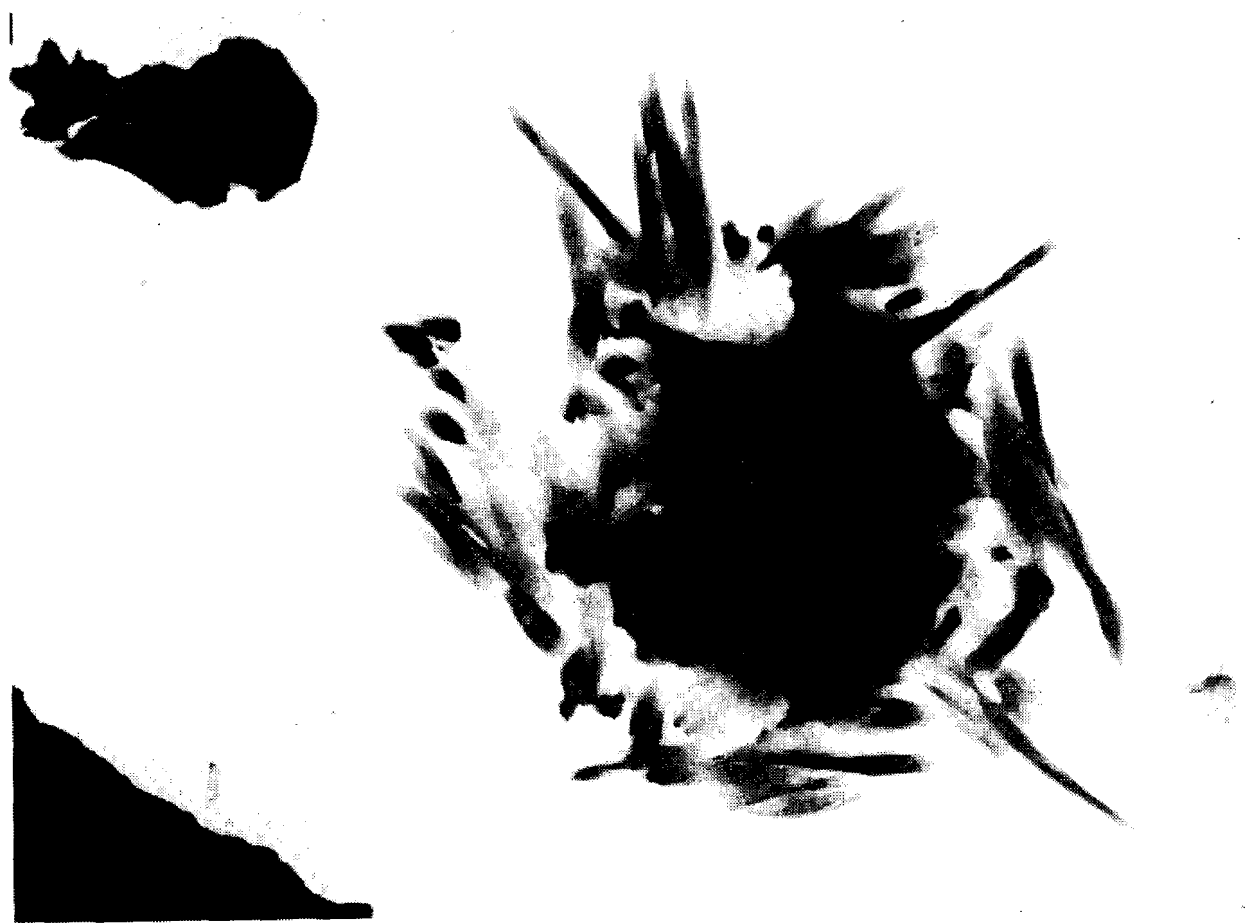


Figure 3. Typical reaction spot of mineral particle coated with a thin layer of nitron. The reaction spot that surrounds the mineral particle, appears as fibers of nitron-nitrate, is indicative of the presence of nitrate on the mineral surface.

REACTION PRODUCTS OF ALTERNATIVE CHLOROFLUOROCARBONS - THE HYDROCHLOROFLUOROCARBONS

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Abstract

The reaction of HCFC-22 (CHClF_2), HCFC-123 (CHCl_2CF_3), and HCFC-141b ($\text{CH}_3\text{CCl}_2\text{F}$) were studied to determine their oxidation products. The reactions were carried out in the laboratory at low ppm reactant concentrations using long path Fourier transform infrared spectroscopy to monitor reactants and products. The laboratory chemical initiation took place by photolyzing chlorine gas in the presence of the HCFC. The chlorine atoms formed in the photolysis of molecular chlorine abstract H atoms from the HCFC. Addition of oxygen to the newly formed radical produces an HCFC peroxy radical that undergoes further reaction. Major carbon-containing products for the reaction of the HCFCs were: $\text{F}_2\text{C}(\text{O})$ from HCFC-22, $\text{CF}_3\text{ClC}(\text{O})$ from HCFC-123, and CO and $\text{FClC}(\text{O})$ from HCFC-141b. The products observed are expected to be similar to those generated under ambient conditions with OH radicals.

Introduction

Stratospheric ozone depletion by chlorofluorocarbons (CFCs) led to the 1987 signing by many countries of the Montreal Protocol. The protocol called for curtailing the production and eventual banning of CFCs over the next decade. The phaseout of CFCs has prompted development of hydrochlorofluorocarbons (HCFCs) that can undergo atmospheric reaction. Replacement HCFCs include HCFC-22 (CHClF_2) for home air conditioners and foam food containers, HCFC-123 ($\text{CHCl}_2\text{F}_3\text{C}$) and HCFC-141b ($\text{CH}_3\text{CCl}_2\text{F}$) as substitutes for CFC-11 (CCl_3F) in the plastic foam industry. Alternative HCFCs are more reactive than CFCs

because the hydrogen atom in their molecular structure can be abstracted by tropospheric hydroxyl (OH) radicals. The subsequent oxidation of the HCFC lead to new compounds having unknown atmospheric fate and effects on stratospheric ozone.

The reactions of HCFC-22, HCFC-123, and HCFC-141b were studied in the laboratory using long path Fourier transform infrared spectroscopy. The initial abstractions of hydrogen atom from HCFC by OH radicals in the atmosphere are simulated in the laboratory using chlorine atoms. Chlorine atoms are produced by the photodissociation of chlorine gas. In the absence of NO_x and other chemical species usually found in the atmosphere all of the oxidation products generated by hydroxyl radical reactions will not be observed in the laboratory with the use of chlorine atoms. Only those products generated under ambient conditions resistant to further reaction are observed in the laboratory system due to the highly reactive nature of chlorine atoms. Therefore only the more stable oxidation products are observed, however, these products are among the products expected to be produced under normal atmospheric conditions.

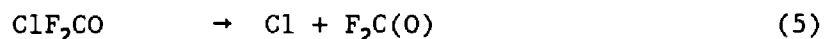
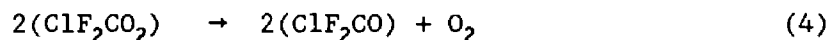
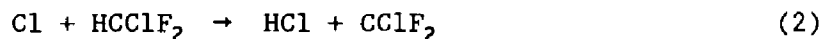
Experimental

The experiments were carried out in a 670 liter photochemical reaction cylindrical chamber constructed of borosilicate glass 9 m in length and 0.3 m diameter. To illuminate the reactants 72 black light and 24 sun fluorescent lamps were evenly spaced around the length of the chamber. The chamber is evacuable and contains an eight mirror optical system set at 144 m for insitu infrared absorption analyses. The chamber was optically coupled to a Digilab Model 80 Fourier transform infrared spectrometer and used a Nernst glower as an IR source and a mercury-cadmium-telluride LN_x cooled detector to cover the spectral range of 650 to 4000 cm^{-1} . Standard spectral absorption techniques were used to obtain data.

The HCFCs of high purity were obtained from E. I. DuPont DeNemours and Company and used without further purification. The HCFCs were added to 650 torr of zero grade tank air in the reaction chamber by injecting μl liquid samples of HCFC-123 or HCFC-141b into a manifold connected to the chamber inlets. Experiments with HCFC-22 a gas at room temperature used a gas-tight syringe to add a pre-determined amount to the manifold. A gas-tight syringe was also used to inject chlorine ($>99.9\%$ pure J. T. Baker Chemical Company) into the manifold. The HCFCs and Cl_2 injected into the manifold were swept into the cell with prepurified tank nitrogen. The initial conditions of experiments were 13 ppm HCFC-220 and 12 ppm Cl_2 , 14 ppm HCFC-123 and 12 ppm Cl_2 , and 15 ppm HCFC-141b and 12 ppm Cl_2 . Experiments were carried out at 700 torr total pressure and $24 \pm 1^\circ\text{C}$. Before irradiation the chamber contents were monitored by obtaining the infrared spectrum of the reactants. After 10 minute periods of irradiation, the chamber contents were again monitored via its infrared spectrum. Substraction of unreacted HCFC from the irradiated spectrum results in an IR absorption spectrum of the products. Authentic samples of F_2CO and $\text{CF}_3\text{C}(\text{O})\text{Cl}$ were obtained from PCR, Inc. and used to identify HCFC reaction products. All reaction products were also identified from literature absorption band values.

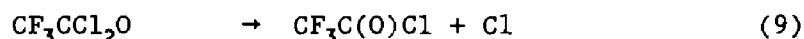
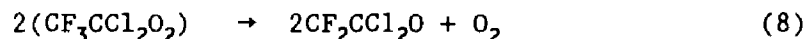
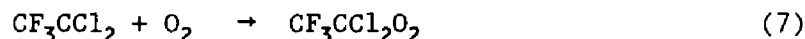
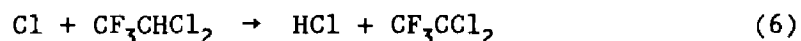
Results and Discussion

In the chlorine initiated oxidation of HCFC-22, the only products observed in the infrared spectra after removal of unreacted HCFC-22 were HCl and F₂CO. The reaction sequence and formation can be explained as follows:



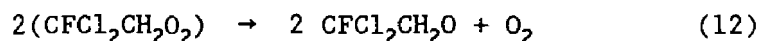
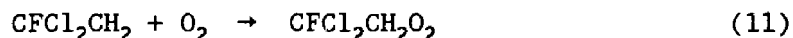
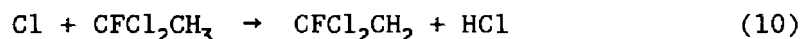
Chlorine atoms formed in reaction 1 abstract a hydrogen from HCClF₂ (reaction 2) to form HCl an observed IR product. In reaction 3 the CClF₂ radical quickly adds O₂ forming a peroxy radical. Because the system does not contain NO or other species which the peroxy radical can react, it reacts with itself as shown in reaction 4 forming the haloalkoxy radical. The product F₂CO observed and identified by its IR absorption bands and comparison with an authentic F₂CO sample forms via the elimination of chlorine atom (reaction 5). Chlorine atom elimination has been reported for other halogenated alkoxy radicals and is a viable mechanism.

The oxidation of HCFC-123 via chlorine initiated reaction produced HCl and CF₃C(O)Cl. Both compounds were identified by IR bands from the literature and the trifluoroacetyl chloride as compared with an authentic sample. The formation of products can be explained by the following reactions. The chlorine atoms formed in reaction 1 abstracts a hydrogen forming HCl and the fluorochloro alkyl radical (reaction 6).

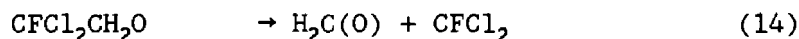
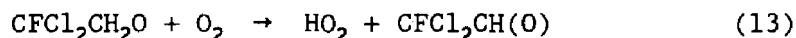


Reaction 7 addition of O₂ to form the peroxyradical, reaction 8 to form the alkoxy radical and the elimination of chlorine atom in reaction 9 are similar to reactions 3, 4, and 5. Thus the main carbon-containing product observed in the oxidation of HCFC-123 is trifluoroacetyl chloride. This compound is stable and is resistant to further attack by chlorine atoms.

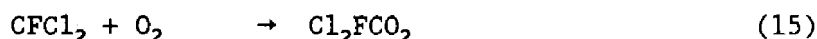
The infrared spectra of irradiated HCFC-141b/Cl₂ mixtures showed the formation of HCl, CO, and FClC(O) as main products. The HCl can be accounted for as in previous HCFC reaction 2 and 6. The resulting HCFC peroxy radical in recombination with itself forms the alkoxy radical (reactions 10, 11, and 12).



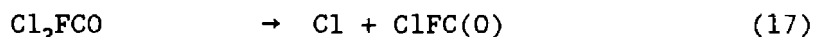
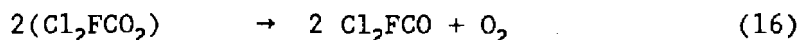
The alkoxy radical can react with O_2 to form an aldehyde or cleave the C-C bond to form $\text{H}_2\text{C}(\text{O})$ and CFCl_2 .



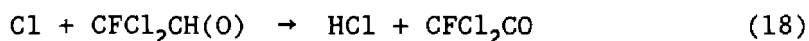
The CFCl_2 radical reacts with O_2 forming a peroxy radical.



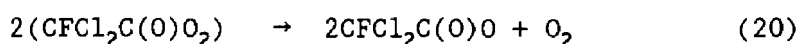
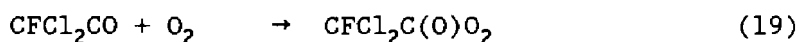
Reaction of two peroxy radicals to form the haloalkoxy radical followed by chlorine atom eliminations results in the formation of fluorochlorocarbonyl $\text{FClC}(\text{O})$.



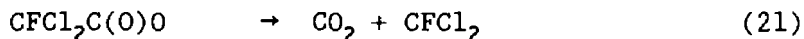
The aldehyde $\text{CFCl}_2\text{CH}(\text{O})$ formed in reaction 13 is reactive toward chlorine atoms in the system and loses its aldehydic hydrogen.



The resulting radical adds O_2 forming a peroxyacyl radical which recombines with itself to form an alkoxy radical.

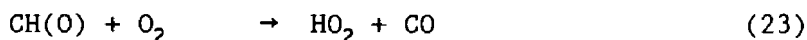
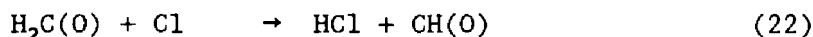


The alkoxy radical dissociates to CO_2 and a CFCl_2 radical.



Chlorofluorocarbonyl is formed from the CFCl_2 radical via reactions 15, 16, 17.

Formaldehyde formed in reaction 14 is quickly oxidized in this highly reactive chlorine system to carbon monoxide an observed product by the following reaction scheme.



As in the case of $\text{F}_2\text{C}(\text{O})$ and $\text{CF}_3\text{C}(\text{O})\text{Cl}$ heterogeneous reactions will be of importance in knowing the atmospheric lifetime and fate of $\text{FClC}(\text{O})$.

Conclusion

The reactions of HCFCs were studied in the laboratory using chlorine atoms to abstract hydrogen atoms as a way of simulating tropospheric OH radical reaction. Due to the very reactive nature of chlorine atoms, the absence in the laboratory experiments of NO and other reactive species usually found in the atmosphere, only those products resistant to further reaction were observed. Chlorine atom initiated oxidation of HCFC-22, HCFC-123, and HCFC-141b resulted in the formation of unique halogen containing carbonyl compounds. The photolysis of chlorine in air and HCFC-22 resulted in the formation of $F_2C(O)$. The chlorine atom initiated oxidation of HCFC-123 led to the formation of $CF_3C(O)Cl$ as the only carbon containing product. Reaction of HCFC-141b resulted in the formation of CO, CO_2 , and $FClC(O)$. More than one reaction sequence may have been responsible for the formation of $FClC(O)$. The formation single carbon atom containing molecules as products indicated C-C bond cleavage in the reaction of HCFC-141b. Future work is needed, especially with heterogeneous reactions, in order to determine the final fate of the oxidation products arising from the degradation of HCFCs.

Disclaimer

Although the research described in this article has been supported by the U.S. Environmental Protection Agency, it has not been subjected to Agency review and therefore does not necessarily reflect the views of the Agency and no official endorsements should be inferred.

**QUANTITATIVE SUPERCRITICAL FLUID EXTRACTION COUPLED ON-LINE
TO CAPILLARY GAS CHROMATOGRAPHY FOR ENVIRONMENTAL APPLICATIONS**

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The usefulness and ease of utilizing supercritical fluid extraction (SFE) directly coupled to capillary gas chromatography (GC) as quantitative or qualitative analytical problem-solving tools will be demonstrated. As an alternative to conventional liquid solvent extractions, SFE presents itself as a means to achieve high extraction efficiencies of different compounds in complex solid matrices in very rapid time frames. Moreover, SFE has an additional advantage of being able to achieve distinct extraction selectivities as a function of the solubilizing power of the supercritical fluid extracting phase. For on-line SFE/GC, the extraction effluent is directly transferred to the analytical chromatograph. On-line SFE/GC involves the decompression of pressurized extraction effluent directly into the heated, unmodified split capillary split injection port of the GC. In this respect, SFE introduction into GC can be used as an alternative means of GC injection, comparable to such modes of injection as pyrolysis and thermal desorption.

INTRODUCTION

Supercritical fluids have been used successfully for years for different industrial applications (1). A large scale application of supercritical fluid extraction (SFE), for example, is to increase crude oil recoveries from porous rocks in oil fields by pumping in gases such as carbon dioxide and nitrogen. In this environment, the pressures and temperatures are high enough that supercritical conditions exist and contribute to enhanced recoveries. Extractions using supercritical fluids are attractive when compared to conventional liquid extractions for a number of reasons. While supercritical fluids have solvent strengths that approach those of liquid solvents, they have lower viscosities (10^{-4} N-sec/m² versus 10^{-3} N-sec/m²) and higher solute diffusivities (10^{-4} c/m²/sec versus 10^{-2} cm²/sec). These properties improve mass transfers from solid or liquid matrices and thus significantly decrease the overall time needed for supercritical fluid extractions. By increasing the density, the solvent strength of a supercritical fluid increases. Therefore, conditions can be optimized for the extraction of a specific solute or class of solutes from a complex matrix by changing the extraction pressure or temperature. Close to the critical point of the supercritical fluid, temperature or pressure changes can change solute solubilities by a factor of 100 or even 1000. By using different supercritical fluids for extractions, such as carbon dioxide, nitrous oxide, and sulfur hexafluoride, preferential extraction can be achieved for different solutes. Moreover, the use of fluids that have low critical temperatures (i.e. CO₂ and N₂O) allow extractions under thermally mild conditions, thereby protecting thermally labile components. Since supercritical fluids, such as CO₂, N₂O and SF₆ are gases at room temperature, off-line component collection or concentration is greatly simplified. Because supercritical fluids undergo expansive (Joule-Thompson) cooling upon decompression, even volatile components can be quantitatively and efficiently collected into solvents off-line after extractions. It is also possible to directly interface supercritical fluid extraction with analytical chromatography, such as capillary gas chromatography (GC) and, supercritical fluid chromatography (SFC). Recent reports have demonstrated the potential of using SFE as an alternative to time consuming, less efficient and less quantitative conventional liquid solvent extraction techniques. Specific solutes ranging from environmental priority pollutants to spices and fragrance components have been qualitatively and quantitatively extracted using supercritical fluids from a variety of liquid and solid sample matrices (2-10). Direct interfaces of SFE to capillary GC and SFC (7-20) have been also demonstrated.

The benefits of directly coupling SFE to GC are that no sample handling is required between the extraction step and the GC separation step and that extraction effluents can be quantitatively and reproducibly transferred for on-the-fly analyses. When employing flame ionization detectors, no detector responses (i.e. solvent peaks) appear for reasonably pure supercritical fluid grade CO₂ or N₂O. This permits the determination of volatile solutes which are often masked by liquid solvents when using conventional extraction techniques. Moreover, when modifiers such as methanol or propylene carbonate, are used to augment the solubilizing power of primary supercritical fluids, they elute as distinct peaks in respective GC or SFC separations. The limitations of coupling SFE to GC are defined by the volatility constraints of higher molecular weight solutes in complex matrices that may not necessarily completely elute from GC columns.

This paper will demonstrate the applicability of SFE/GC techniques towards the quantitative and qualitative characterization of some environmental matrices.

EXPERIMENTAL

On-line SFE/GC was performed on a Suprex Model SFE/50 stand-alone extractor equipped with an electronic Valco four-port high pressure selector valve and a Hewlett-Packard Model 5890 gas chromatograph equipped with a split/splitless capillary injection port and flame ionization detector.

Figure 1 shows a schematic diagram of the SFE/GC interface. The Suprex SFE/50 extractor consists of a 250ml syringe pump with pressure limits up to 500 atm.

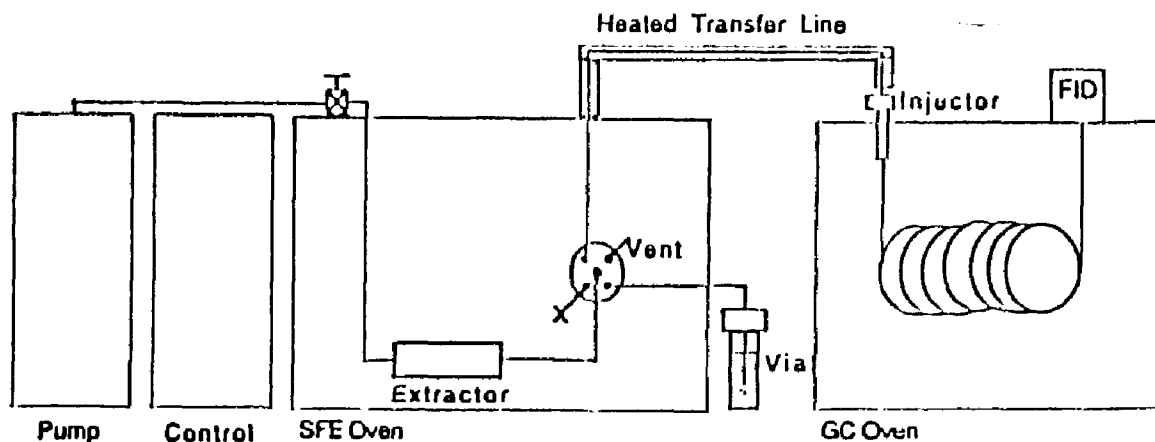


Figure 1. On-Line SFE/GC Schematic Diagram

The oven of the extractor was large enough to accommodate multiple extraction vessels or extraction vessels up to 50 ml in volume. The electronically actuated Valco four-port selector valve was used to perform the static and dynamic extractions and to divert the extractor effluent flow into the injection port of the GC. The controlling software of the Suprex SFE/50 permitted the automatic operation of the four-port selector valve and automatically initiated the run on the GC after dynamic transfer of the extractor effluent. Both 1/32 inch O.D. X 0.007 inch I.D. stainless steel and 15 or 25 micron I.D. fused silica tubing have been used as transfer lines between the SFE/50 and the 5890 gas chromatograph. When stainless steel tubing was used, it was necessary to restrict the flow by crimping to allow a flow of 40-80 ml/minute of expanded decompressed gas at the specified extraction pressure. The transfer line tubing was inserted 35-40 mm directly into the split/splitless capillary injection port which was kept at 225°C to minimize the Joule-Thompson cooling which occurred when the supercritical fluid phase decompressed. For purposes of solute focusing, it was also necessary to cryogenically cool the gas chromatographic oven. The oven was kept cool long enough to allow the dynamic transfer of the respective vaporized solutes onto the head of the capillary gas chromatographic column. The level of cooling depended on the volatility of the solutes of interest. Generally, the GC oven was never cooled below -50°C which would cause freezing of the decompressed carbon dioxide.

RESULTS AND DISCUSSION

The use of SFE on a quantitative analytical scale presents a number of distinct advantages when compared to conventional solvent extractions. Depending on the sample matrix, the nature of supercritical fluids allows for rapid extractions in usually less than one hour with high extraction efficiencies. Moreover, the ability to transfer the SFE effluent to a GC or SFC in an automated fashion permits sensitive quantitative or qualitative determinations of solutes in different solid or liquid matrices.

The quantitative reproducibility of on-line SFE/GC was investigated by performing comparative triplicate analyses using SFE with split GC and flame ionization detection and conventional syringe split GC injections of methylene chloride extracts of the spiked clay shown in Figure 2.

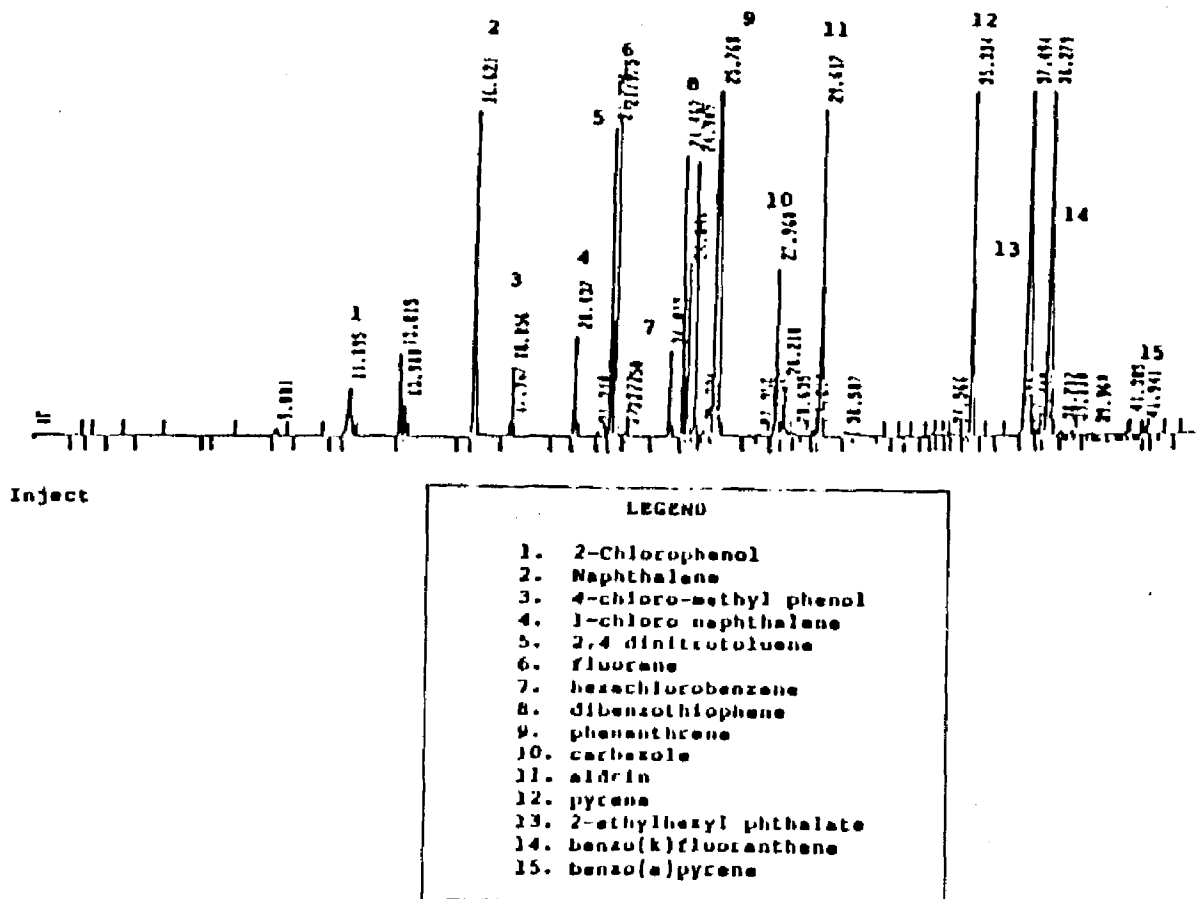


Figure 2. SFE/GC-FID Analysis of Priority Pollutants in Clay. GC temperature program: 0°C (20 minutes) programmed to 300°C at 7°C/minutes.

The operating conditions for SFE included 400 atm pressure of supercritical CO₂ at 60°C for 20 minutes using 650mg quantities of clay in a 500 microliter SFE vessel. A 50 meter X 0.2 mm I.D. methyl silicone (PONA) capillary GC column was used to provide the separation. The SFE effluent was transferred directly to the capillary GC injection port using a fused silica 15 micron I.D. transfer line. All peak identities were confirmed using a mass spectrometer. Table I lists the peak area reproducibility results for selected priority pollutants in the clay.

Table 1. Comparison of Peak Area Reproducibility for Priority Pollutants in Spiked Clay with On-Line SFE/GC and Conventional GC Split Injections.

Priority Pollutant	% RSD* SFE/GC	% RSD* Split GC	Concentration (ng/ul)
2-chlorophenol	1.8	2.0	50
Naphthalene	2.1	4.6	200
1-chloronaphthalene	5.6	8.1	60
Hexachlorobenzene	5.8	7.8	50
Phenanthrene	4.0	3.8	300
Pyrene	4.2	5.6	200
Benzo(a)pyrene	5.5	6.4	20

*Based upon raw peak areas resulting from an average of three replicates.

As can be seen, the SFE/GC results compared favorably with those obtained by conventional syringe GC injections. Moreover, the percent relative standard deviations for the SFE/GC-FID results include contributions from sample inhomogeneity, weighing, and technique errors as opposed to only injection and integration errors for the methylene chloride extract injections. It was also very important to thoroughly grind the clay sample before loading the SFE vessel to obtain consistent results. Certain matrices, such as some clays, have sufficient density to trap certain solutes for longer periods of time thereby disrupting the efficiency of the extraction process. Figure 3 shows a SFE/GC-FID chromatogram of another environmentally important sample matrix namely, marine sediment.

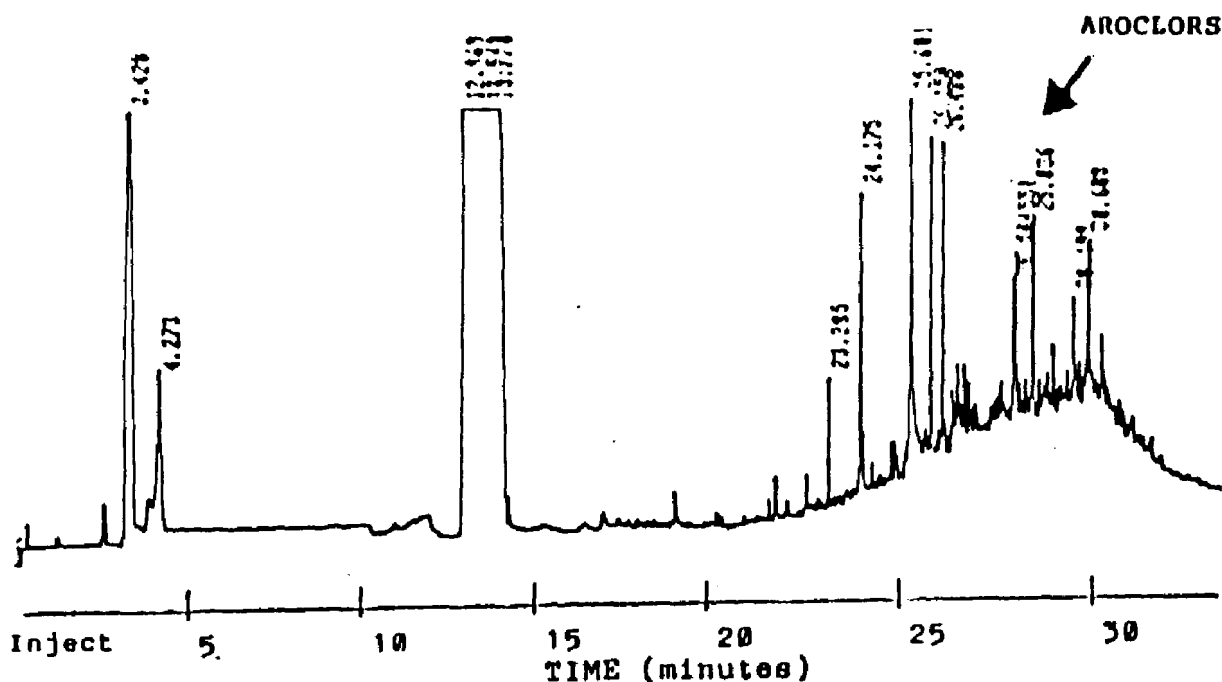


Figure 4 with the determination of aromatics and chlorinated aromatics in contaminated soil which was taken from a spill site.

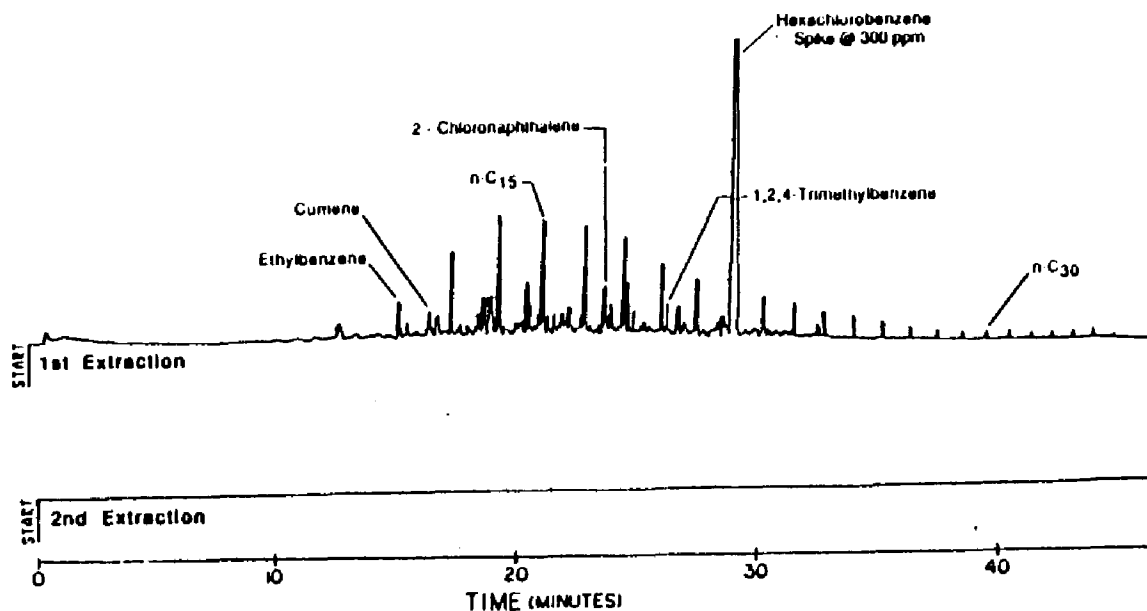


Figure 4. SFE/GC-FID Analysis of pollutants in soil. GC temperature program: 30°C (7 minutes) programmed to 310°C at 7°C/minute.

Approximately 170 mg of the soil was extracted in a 0.5 ml vessel at 375 atm using supercritical CO₂ at 50°C for 30 minutes. A 30 meter x 0.25 mm I.D. DB-Wax capillary column was used to provide the GC separation. Hexachlorobenzene was used as an internal standard which was spiked directly into the soil before extraction. Table II lists the quantitative results for replicate analyses of the soil.

TABLE II. Replicate SFE/GC-FID Determinations of Aromatics and Chlorinated Aromatics in Contaminated Soil

COMPOUND	CONCENTRATION (PPM)*			
	1	2	3	4
ethylbenzene	44	40	42	43
cumene	30	30	32	34
2-chloronaphthalene	51	50	51	48
1,2,4 trimethylbenzene	25	26	29	24

*Based upon internal standard calculations

CONCLUSIONS

The use of directly coupled SFE/GC as an analytical techniques has shown excellent potential for the quantitative and qualitative characterization of different solutes in different matrices of environmental significance. Using on-line SFE/GC, an entire analysis which includes the extraction, concentration, clean-up, and analytical separation steps, can be accomplished in usually less than one hour. Selective extractions can also be performed by varying parameters such as pressure, temperature, and type of supercritical fluid extracting fluid. Moreover, the analytical versatility and flexibility of the technique can be further enhanced by the utilization of such chromatographic detectors as mass spectrometry, electron capture, nitrogen-phosphorus, and sulfur-specific.

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THE ROLE OF SFE IN METHODS FOR THE ANALYSIS OF TOXIC COMPOUNDS

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Abstract

The recoveries of ^{14}C -labelled γ -BHC, hexachlorobiphenyl, ethyl parathion, and anthracene from Tenax-GC and four polyimide sorbent materials were studied using off-line supercritical carbon dioxide extraction (SFE) and thermal desorption methods. SFE was superior to thermal desorption. On-line SFE/GC analysis both with and without an intermediate Tenax-GC adsorption step was studied using a mixture of nonradiolabelled pesticides. The addition of the Tenax-GC step allowed for larger extraction volumes than were possible using direct SFE/GC with analyte transfer into the chromatographic column. The intermediate trapping step also improved the chromatographic efficiency relative to direct SFE/GC. Replicate analyses indicated variabilities less than 3% relative standard deviation.

Introduction

As more becomes known about the toxic effects of organic compounds present in ambient air, the identification and quantification of these compounds, often present in trace quantities, are more important than ever to understand the extent and magnitude of the exposure problem. Organic compounds in air range from those that are very volatile (VVOC, e.g., 1,1,1-trichloroethane) to volatile (VOC, e.g., chlorobenzene) to semi-volatile (SOC, e.g., pesticides and phthalates). Over the years, many analytical methods tailored to specific volatility categories have been developed. Collection of air into evacuated canisters with subsequent gas chromatographic analysis of the contents using mass spectrometric detection (GC/MS) has been applied to VVOCs. As the volatilities of the compounds decrease, they are present in the atmosphere at lower levels and the analysis of a small volume of air does not provide the necessary sensitivity. As a result, methods were developed that rely on the selective adsorption of the organic compounds as large volumes of air are drawn through an adsorbant-filled tube. Tenax-GC is widely used as a sorbent to collect VOCs with the analysis performed on-line with a GC/MS through the use of thermal desorption of the retained chemicals¹. For SOC's such as PCBs, pesticides, and phthalates, polyurethane foam (PUF)² or XAD resin³ is used for collection. The recovery of these semi-volatile analytes requires solvent extraction methods. GC/MS analysis is performed on the extract.

Although such preconcentration techniques are very powerful, they are not without limitations. One problem is found in the selectivity of Tenax-GC; this material retains nonpolar compounds to a much greater extent than polar compounds. If quantification of polar compounds is desired, the volume of air sampled needs to be reduced to avoid "breakthrough" of these polar compounds and this can limit the sensitivity of the method. The utilization of sorbents more polar than Tenax-GC could help circumvent this problem; four polyimide sorbents synthesized at RTI and found suitable for use with thermal desorption/GC have been reported⁶. The competitive effects of adsorption for polar and nonpolar analyte vapors on the polyimides were studied as a means of improving the sampling methods for polar analytes⁴.

A second problem is found when the thermal desorption of strongly adsorbed compounds is attempted. Thermal desorption can fail because a temperature sufficient to desorb the analyte might also destroy the sorbent, the analyte, or both. In addition, if a compound is thermally unstable, thermal desorption can invalidate quantification and introduce artifacts even if the analyte is only weakly adsorbed.

Ongoing research in our laboratory has been directed at the utility of supercritical carbon dioxide extraction for environmental analysis. The high solvating capability of the fluid can facilitate the recovery of strongly adsorbed analytes from sorbents for subsequent collection and analysis. The extract can either be expanded into a solvent to provide a solution that can be analyzed later (off-line) or it can be introduced directly into a chromatographic system for on-line analysis. On-line SFE methods can preserve the favorable concentration factors of thermal desorption GC and provide for methods with very low limits of detection over an extended range of volatilities. Because the critical temperature of CO₂ is approximately 31°C, high temperatures can be avoided and thermally-induced decomposition of analytes is not a concern. In addition, SFE can result in methods devoid of large volumes of organic solvents. For example, methods that utilize Soxhlet extraction for the recovery of analytes (e.g., PUF) require large volumes of organic solvent most of which is sent to waste

or into the atmosphere during volume reduction steps.

Work presented in this paper demonstrates the utility of SFE in the recovery of low levels of semivolatile compounds of environmental concern from Tenax-GC and four polyimide sorbents. Additional preliminary work will also show how such sorbents can be used to permit the on-line extraction and GC analysis of SOC's where large extraction volumes might be needed.

Experimental Methods

Solutions of γ -[$^{14}\text{C}(\text{U})$]BHC (1,2,3,4,5,6-hexachlorocyclohexane), [9- ^{14}C]anthracene, [ring-2,6- ^{14}C]parathion and [$^{14}\text{C}(\text{U})$]-2,3,5,2',3',5'-hexachlorobiphenyl were prepared individually in dichloromethane to a concentration of between 11 and 40 ng per microliter. One microliter aliquots were introduced into a GC injector and swept with helium onto a cartridge (4.8 cm long x 4.6 mm ID x 0.25 in OD; 0.8 mL total volume) packed with 40-60 mesh Tenax-GC or one of the polyimides as previously described^{5,6}. The cartridge was then extracted with CO_2 at 3000 psi and 40°C (density of approximately 0.85 g/cm³) and the effluent was expanded into a scintillation vial containing 15 mL scintillation cocktail. Alternatively, the cartridge was left in the GC, heated to 250°C, and purged with helium at 1.5 mL/min for 8.5 min or 6.4 mL/min (Tenax-GC) or 12 mL/min (polyimides) for 10 min. The 1.5 mL/min flow for 8.5 min purged the sorbent with the same number of column volumes as is used in routine application of Tenax-GC thermal desorption where the sorbent cartridge is ten times larger. The effluent was directed through a heated transfer line into a vial containing scintillation cocktail; cocktail was used to rinse any residual compound from the transfer line into the vial. In each case, recoveries were determined from radioactivity recovered from a known mass of compound deposited into the thermal or SFE desorption system in the absence of a sorbent.

The work with SFE/GC and SFE/SFE/GC was conducted as follows. A Valco HPLC injector fitted with a 500 nL rotor was placed in-line and before the 0.41 mL SFE cell which was filled with sea sand and held at 50°C in a modified Lee Scientific Model 501 SFE/SFC system. The valve allowed for the reproducible introduction of a methanol solution of pesticides (approximately 100 ng each) into the cell so that SFE conditions could be mimicked. The pesticides used were molinate, propoxur, atrazine, γ -BHC, triallate, terbutryin, ethyl parathion, γ -chlordane, and phosmet. The outlet of the SFE cell was directed through a multiport switching valve to a fused silica restrictor (13 cm x 25 μm ID). In the direct SFE/GC configuration, the restrictor was placed into the first few cm of a DB-5 capillary column (30 m x 0.32 mm ID) at ambient temperature. In the SFE/SFE/GC configuration, the effluent of the SFE cell was expanded onto the head of a column comprised of a steel tube (6 cm x 4 mm i.d.) with fritted column end-fittings and packed with 0.14 g Tenax-GC. The Tenax-GC cell was also held at 50°C. After this extraction and deposition, supercritical CO_2 was used to extract the Tenax-GC in the direction opposite to that of analyte deposition. This effluent was expanded through another restrictor (13 cm x 25 μm ID) into the first few cm of the GC column, again at ambient temperature, as in the SFE/GC experiment. After the SFE step(s), the column was purged with helium and the temperature was programmed to effect separation. Flame ionization detection (FID) was used and data were collected by either an HP 3390A integrator or a Nelson Analytical Data system. All extractions were conducted at 400 atm resulting in CO_2 extraction densities of 0.928 g/cm³.

Results

Polymer Desorption

SFE Desorption An initial study of the total radioactivity recovered as a function of CO₂ volume was performed for each compound on each sorbent. From these data, we chose extraction volumes for each analyte/sorbent combination for use in the experiments to determine recoveries. The results of the recovery experiments are shown in Table I. The analytes were recovered to a higher extent using a smaller extraction volume from Tenax-GC than from the polyimides. This is consistent with earlier work⁷ where lower GC retention volumes were measured on columns packed with Tenax-GC than on those packed with any of the polyimides.

Thermal Desorption The recoveries measured using thermal desorption are shown in Table II. For these semivolatile test compounds, thermal desorptions using 50 column volumes of helium provided very poor recoveries from all of the sorbents. Increasing the desorption volume and time led to improved recoveries of BHC and anthracene from Tenax-GC while the recoveries for hexachlorobiphenyl and parathion were not changed. The results for the polyimides are indicative of the tenacity of these sorbents for the test compounds. For the low volume desorptions, none of the compounds was recovered well. Using the more rigorous desorption conditions, the recoveries of the analytes improved; only BHC was well-recovered from polyimides 119, 149, and 115.

SFE/GC

Direct SFE/GC experiments using extraction times of 7 and 10 minutes (8 and 11 column volumes, respectively) revealed that better recoveries and peak shapes were obtained at the shorter times suggesting that the analytes were deposited and then lost at longer extraction times. The flow rate of CO₂ during extraction was 81 mL/min at ambient conditions. A lower trapping temperature might improve this situation but was not tried because the goal here was to determine if the presence of the secondary Tenax-GC trapping step could minimize the problems associated with the longer time of the first extraction step. Replicate SFE/GC analyses provided percent relative standard deviations (%RSD) of less than 3% using an extraction time of 7 minutes. Figure 1 shows the chromatogram obtained after SFE/SFE/GC of the pesticide mixture. In this case, the time of extraction from the Tenax-GC was 7 minutes and the time of extraction from the sand was 15 minutes. The use of sand extraction times up to 30 minutes did not affect the recoveries or chromatographic efficiencies as long as the Tenax-GC extraction time was maintained at 7 minutes. This allows for a great deal of flexibility in the first extraction time as long as the analytes of interest are well retained by the Tenax-GC. For compounds of relatively low volatility, this should not be a problem. A gas chromatogram of the test pesticides obtained using conventional splitless/split injection is shown in Figure 2 for comparative purposes. Although some broadening of the chromatographic peaks is seen in the SFE/SFE/GC case of Figure 1, relative to Figure 2, the efficiencies of the separations shown in Figure 1 are certainly adequate for most purposes and could probably be improved upon through a careful optimization of flow rate and column temperature during extraction of the Tenax-GC cartridge. Replicate analyses using SFE/SFE/GC provided %RSDs of less than 3%.

Table III shows a comparison of the chromatographic peak area to height ratios for each of the pesticides for both SFE/GC and SFE/SFE/GC. This ratio is indicative of chromatographic efficiency, with a low ratio reflecting a higher efficiency. The extraction times for both SFE/GC and

SFE/SFE/GC were 7 minutes at the same extraction flow rate, and thus differences reflect the effect of the Tenax-GC in the system. It can be seen that, in all cases, the presence of the Tenax-GC resulted in sharper peaks. This is presumably due to the accumulation of the analytes at the head of the Tenax-GC cartridge. When the Tenax-GC is back-extracted, the analytes are introduced into the column as a tight band. In SFE/GC, the analytes were introduced onto the column over a longer time because of the band spreading that occurred during the migration through the sand. Such an effect would be expected to be more pronounced in a real extraction situation where desorption of the analytes from the matrix would take place over a longer time with the result that they would be spread out even more. The use of a secondary sorbent can minimize this effect.

Conclusions

The use of polymeric sorbents in conjunction with SFE can allow for the recovery of less volatile and more polar analytes than is possible using thermal desorption methods. In addition, the use of the sorbent Tenax-GC in an on-line SFE/GC analysis scheme (SFE/SFE/GC) can provide greater flexibility in the extraction of the sample than can direct SFE/GC analysis of semivolatile organic compounds. The use of on-line SFE/GC methods has the potential to allow for the collection of smaller samples (smaller air sampling volumes) and, because the entire extract is analyzed, to lower the limits of detection of the analytical method.

Acknowledgements

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TABLE I. PERCENT RADIOACTIVITY RECOVERED BY
SUPERCRITICAL CO₂ DESORPTION

Compound	Sorbent				
	Tenax-GC	PI-109	PI-119	PI-149	PI-115
γ -BHC	100(14) ^a	100(45)	86(30)	92(30)	99(30)
hexachlorobiphenyl	95(14)	72(60)	79(30)	77(30)	85(30)
parathion	92(14)	58(101) ^b	74(45) ^b	76(45) ^b	77(45) ^b
anthracene	81(14)				

^a Approximate number of column volumes of CO₂ used at 3000 psi and 40°C.

^b Recovery not determined.

TABLE II. PERCENT RADIOACTIVITY RECOVERED
USING THERMAL DESORPTION AT 250°C

Compound	Tenax-GC		PI-109		PI-119		PI-149		PI-115	
	50 ^a	260	50	500	50	500	50	500	50	500
γ -BHC	27	88	1	50	6	88	9	83	22	94
hexachlorobiphenyl	13	13	1	14	16	21	17	57	32	59
parathion	12	12	8	3	3	9	8	25	12	36
anthracene	10	99	8	3	8	6	11	26	14	18

^a These values indicate the number of column volumes of helium used for the desorption.

TABLE III. CHROMATOGRAPHIC EFFICIENCY OF PESTICIDE SEPARATION
AS REFLECTED BY AREA/HEIGHT RATIOS

Compound	SFE/GC ^a (%RSD)	SFE/SFE/GC ^b (% RSD)
Molinate	7.4 (3.9)	5.4 (4.9)
Propoxur	7.6 (4.7)	5.4 (7.5)
Atrazine	8.2 (1.2)	5.8 (6.5)
γ -BHC	8.4 (3.8)	6.2 (7.4)
Triallate	7.4 (5.6)	5.7 (6.3)
Terbutrin	8.5 (4.2)	5.8 (1.0)
Ethyl parathion	8.3 (5.7)	6.0 (5.8)
γ -Chlordane	8.9 (4.3)	6.3 (6.0)
Phosmet	12.8 (3.7)	8.8 (1.3)

^a Extraction time of 7 minutes; triplicate analysis.

^b Extraction of sand for 15 minutes followed by 7 minute extraction of Tenax-GC; triplicate analysis.

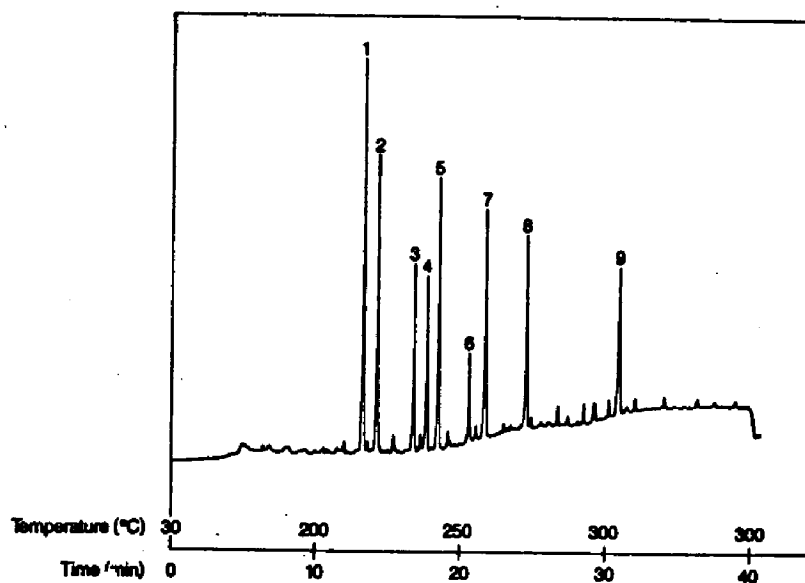


Figure 1. SFE/SFE/GC chromatogram of pesticide test mixture. Compound identifications are (1) molinate, (2) propoxur, (3) atrazine, (4) γ -BHC, (5) triallate, (6) terbutyrin, (7) ethyl parathion, (8) γ -chlordane, (9) phosmet. Conditions as described in the text.

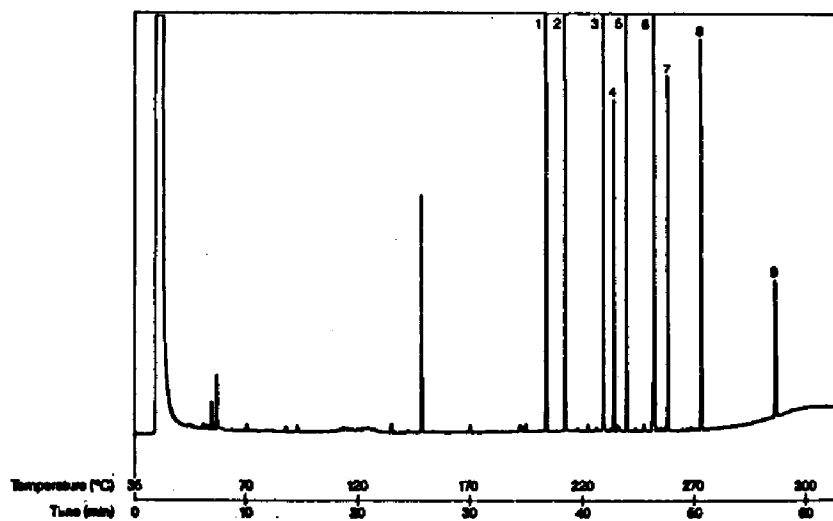


Figure 2. GC chromatogram of the pesticide test mixture after splitless/split injection. The large peak before molinate is either an impurity or thermal decomposition product of propoxur.

SUPERCRITICAL FLUID EXTRACTION OF POLYURETHANE FOAM SORBENTS

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Polyurethane foam (PUF) sorbents have become widely used for air sampling because of their low resistance to air flow and ease of handling. However, the usefulness of PUF is limited by the time consuming liquid solvent extraction required. Supercritical fluid extraction (SFE) of PUF is a rapid alternative to conventional liquid solvent extraction. SFE can achieve quantitative extraction of polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAH) ranging from naphthalene to perylene, heteroatom-containing PAH, *n*-alkanes ranging from C₁₂ to C₂₄, and organochlorine pesticides from PUF in 10-20 minutes. In addition, the direct coupling of SFE with gas chromatography (SFE-GC) is possible. SFE-GC quantitatively transfers all compounds collected on the sorbent plug to the gas chromatographic column for analysis. Thus, SFE-GC can reduce the mass of sample needed by two orders of magnitude, and it can also decrease sampling time by two orders of magnitude. The application of SFE and SFE-GC of PUF for the rapid extraction and analysis of variety of semivolatile organic compounds will be demonstrated.

Introduction

Polyurethane foam (PUF) has become a widely used sorbent for the collection of semivolatile organic compounds. Polyurethane foam has a low resistance to flow, is inexpensive and easy to use, and is effective at collecting a broad range of semivolatile organic compounds. However, traditional liquid extraction techniques that are used to extract PUF, such as Soxhlet extraction and sonication, are very time consuming, error prone, and require large volumes of high purity solvents.

Supercritical fluids have many advantages over liquid solvents for extraction of PUF. Supercritical fluids have lower viscosities and higher solute diffusivities than liquid solvents, resulting in improved mass transfer, and therefore a shorter extraction time. The solvent strength of a supercritical fluid can be controlled by changing the pressure (and therefore, its density), in order to gain selectivity in the extraction process. Supercritical fluids such as CO₂ and N₂O have low critical temperatures (32 °C), making them ideal for extraction of thermally labile solutes or sorbents. Fluids such as CO₂ and N₂O are also gases at ambient temperature and pressure, which simplifies solvent removal and sample concentration. Also, the direct coupling of supercritical fluid extraction to gas chromatography (SFE-GC) is possible. Coupled SFE-GC has the potential to reduce the volume of air that one needs to sample for collection of semivolatile organics by two orders of magnitude, thus decreasing sampling time by two orders of magnitude.

EXPERIMENTAL METHODS

Extractions were performed using either a SFT Inc. model 250-TMP syringe pump (Salt Lake City, UT) or an ISCO model μ LC-500 syringe pump (Lincoln, NE). Supercritical fluid grade CO₂ and N₂O in aluminum cylinders was obtained from Scott Specialty Gases. Extraction cells were constructed from Parker brand stainless steel fittings¹. Supercritical pressures were maintained inside the extraction cell by using 15 cm lengths of 20-30 μ m i.d. X 150 μ m o.d. fused silica tubing (Polymicro Technologies, Phoenix, AZ). Extraction temperature was maintained by inserting the extraction cell into a thermostatted tube heater. Extracted compounds were collected by inserting the outlet of the fused silica restrictor into a vial containing ca. 4 ml of hexane. Approximately 400 ng of PCB congener 204 (2,2',3,4,4',5,6,6'-octachlorobiphenyl) was spiked into each vial before the extraction as an internal standard. Coupled SFE-GC experiments were performed by inserting the fused silica restrictor directly into the capillary gas chromatographic column through the on-column injection port¹. Extracted analytes were cryogenically trapped at 5

°C in the gas chromatographic oven. After completion of the extraction, the restrictor was withdrawn from the injection port and gas chromatographic analysis proceeded in a normal manner. All GC/MS and SFE/GC/MS analysis were performed on a Hewlett-Packard 5985B GC/MS system using electron capture negative ionization (ECNI). Ion source temperature was 100°C and the reagent gas was methane at a source pressure of 0.45 torr. The GC/MS was equipped with a 30 m DB-5 (250 μ m i.d, 0.25 μ m film thickness) capillary column (J&W Scientific, Folsom, CA).

RESULTS

The ability of supercritical CO₂ to recover a variety of organochlorine pesticides from PUF is shown in Table 1. Approximately 100 ng of each compound was spiked into the center of the PUF plug. After allowing the solvent to evaporate, the plug was extracted for 10 minutes with CO₂ at 300 atm and 50 °C. These results show that supercritical CO₂ is able to rapidly and quantitatively remove these compounds from the PUF matrix.

Off-line extractions can be performed using a relatively high flow rate (ca. 1 ml/min with a 30 μ m) restrictor. However, the extraction flow rate is limited during a coupled SFE/GC/MS by the efficiency of the cryotrapping step and the pumping speed of the mass spectrometer. A practical limit for on-line SFE/GC/MS is approximately 200 μ l/min of liquid flow. Therefore, it takes roughly 5 times longer to pump an equivalent volume of supercritical fluid through the extraction cell during a coupled SFE/GC/MS experiment. In order to minimize the time required for the extraction step during future on-line analyses, we examined short extraction time intervals to determine what percentage of each analyte is extracted over a given time period. Figure I shows that from 80-95% of each of the test compounds was extracted in the first two minutes with both supercritical N₂O and CO₂. The remaining fraction was collected in the next two minute interval, leaving less than 1% of analyte for the final six minutes of the extraction. These results imply that these compounds could be quantitatively extracted from PUF in ca. 15-20 minutes during a coupled SFE/GC/MS experiment.

SFE/GC/ECNI/MS analysis of a PCB standard (one congener from each level of chlorination from tetrachloro through decachlorobiphenyl, ca. 250 pg/congener) spiked onto PUF showed mixed results. Comparison of the amount of each individual congener detected in two consecutive 20 min extractions of the same sample indicated that approximately 90-95% of each congener had been extracted in the first 20 minutes. However, comparison with an external standard

associated with individual measurements. The QA/QC results further emphasized the need to consider all the data from the study in making decisions.

Many of the testing results were "not detected," and the measured concentrations were all less than 0.5 ppmv. The data analysis focused on comparing the study area results to those for the control area and on comparing indoor and outdoor data sets. These comparisons were critical, especially in presenting data to the community, since many of the results were not zero. The outdoor and control area data sets provided perspective with which to evaluate the study area indoor results. As shown in the example in Table I, when whole data sets were examined, the study area sample concentrations were very similar to those measured in the control area samples and in the samples from the outdoor locations. If a subsurface source were contributing significantly to the indoor concentrations, the study area indoor levels would be expected to be higher than those in the control area and higher than the outdoor levels. A nonparametric statistical method, along with a standard t-test, was used to compare the study area and control area indoor and outdoor data sets for individual target compounds to determine whether there were any significant differences between these sets that might indicate a subsurface impact. Both types of statistical analyses produced the same results: the study area indoor levels were not significantly higher than the study area outdoor levels for any target compounds and were not significantly higher than the control area levels for most compounds. The test also indicated that any differences between the study area and control area indoor air were less than the outdoor differences between the two areas. The nontarget compounds detected in the study area indoor samples were similar in type and level to those detected in the control area and were not similar to the compounds that had been measured in ground water on site.

The results suggested that when concentrations of target compounds were measured in the study area structures, their presence was likely associated with household product use, outdoor air, or possibly natural gas, rather than with a subsurface source. On an individual structure basis, indoor concentrations were very similar to the corresponding outdoor concentration in most cases, and the houses where the indoor levels were higher than the outdoor levels were scattered throughout the testing area and were not clustered in one location.

Conclusions and Recommendations

Results of two exposure assessments conducted at apparently similar sites demonstrated the importance of developing a site-specific technical approach. For Site 1, the available data and observations suggested that a subsurface impact to residential indoor air was possible, or even likely; and for certain structures, the testing results indicated an impact. The technical approach emphasized full characterization of the subsurface contamination, investigation of indoor point sources, and speciation analysis to recognize the "fingerprint" species and ratios. The priorities of the facility and the regulatory agencies to move rapidly toward any necessary mitigation were addressed in developing this technical approach, which provided information key to the design and scoping of mitigation measures in individual structures and recovery of the liquid hydrocarbon.

The available information for Site 2 indicated that a measurable impact was not likely, and that the target compounds were very common solvents that could be expected to occur in the outdoor air and in household chemical products. The technical approach therefore emphasized simultaneous outdoor testing, so that any measured indoor levels could be

evaluated with respect to the corresponding outdoor levels; testing in a control area to provide data representing typical levels of the target compounds in a residential setting; and inventories of household chemical products in the tested structures. Since all measured concentrations were expected to be very low, the study was designed to collect representative sets of data that could be compared to determine any impact. Results of the testing did not indicate any subsurface influence on indoor levels, as the levels measured in the study area indoor and outdoor samples, and in the control area samples, were all similar. Detection limit studies and thorough QA/QC sampling and analysis were conducted to ensure that the potential for false positive and false negative results, and the degree of variability in the data, were fully assessed. The outdoor air and control area data were critical in providing perspective, mainly to prevent the incorrect interpretation of any measured concentration as indicative of an impact. The number of structures tested was more a function of assurance for the residents than a scientifically-based, representative sampling scheme.

Neither of these approaches would have been well-suited to the other site, and considering these examples emphasizes that no single, or "generic" technical approach will be appropriate for exposure assessment at a given site. In these examples, point source sampling and "fingerprinting" chemical species would not have been effective measures for Site 2 due to the very low levels and mixtures of subsurface compounds. Conducting such sampling and analysis would have been an unnecessary expense. Similarly, for Site 1, a study design focused on comparison of whole data sets - for instance comparing all of the study area data to all of the control area data - would not have allowed prioritization of individual structures and areas for further investigation and mitigation.

In general, it is recommended that the technical approach for each residential indoor air investigation be tailored for the specific site by considering such important factors as:

- subsurface conditions,
- types, toxicities, and levels of subsurface contamination,
- other potential sources of similar compounds,
- characteristics of the residential structures,
- outdoor ambient air conditions,
- initial indoor observations, and
- priorities of the regulatory agencies and the community.

Making full use of available information in the categories listed here will ensure that resources can be focused on the most critical elements of the investigation to produce scientifically defensible and cost-effective assessment of the exposure potential for the site.

Table I
Average subsurface and indoor/outdoor air concentrations for
representative target compounds in two studies designed to
assess subsurface impacts to residential indoor air.

SITE 1	Average Concentrations in Parts Per Million				
	TNMHC	Benzene	Isopentane	2-Methyl-2-butene	Ratio*
Indoor Air					
Level 1 Structures PS	9.1	0.76	13	14	1.1
Rm Amb.	3.3	0.048	0.33	0.43	1.1
Level 2 Structures PS	23	0.55	2.5	3.0	1.2
Rm Amb.	2.2	0.033	0.23	0.23	0.87
Other Structures PS	24	NA	0.038	0.0	0.0
Rm Amb.	0.68	NA	0.018	0.0054	0.58
Control Structure Rm Amb.	1.2	0.0038	0.13	0.0018	0.015
Outdoor Air	0.16	0.00097	0.005	0.003	1.3
Shallow Soil Vapor	8,100	180	800	700	1.1
Vapor Above Shallow Ground Water	29,000	732	2,800	3,200	1.2

SITE 2	Average Concentrations in Parts Per Million			
	Acetone	Cyclohexane	Benzene	Trichloroethene
Indoor Air				
Study Area	0.029	0.0068	0.0010	0.00031
Control Area	0.047	0.0064	0.0014	0.00033
Outdoor Air				
Study Area	0.030	0.0086	0.00085	0.00034
Control Area	0.011	0.0020	0.00064	0.00030
Shallow Soil Vapor				
Study Area	0.016	0.0004	0.0010	NA
Control Area	0.006	0.009	0.0023	NA
Shallow Ground Water	<0.05	<0.05	<0.05	<0.05

TNMHC - Total non-methane hydrocarbons.

PS - Point source measurement.

Rm Amb - Room ambient measurement

NA - Not available

Average - One-half the detection limit was used for "not detected" results in calculation.

* - Ratio refers to the ratio of 2-methyl-2-butene concentration to isopentane concentration in individual samples.

VOLATILE ORGANIC COMPOUNDS IN THE ATMOSPHERE OF A NEWLY CONSTRUCTED RESIDENCE

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A newly constructed house located in Princeton N.J. was chosen to determine the initial concentrations of some selected volatile organic compounds (VOC) and total hydrocarbons and to follow the decay of these levels as construction materials out-gassed. A Tenax adsorbent trap sampler was used to collect samples in and out side of the house simultaneously during the first six months after the house was occupied. Thermal desorption with capillary GC and GC/MS were used for quantitative and qualitative analysis. The concentration distribution of more than 12 compounds both inside and outside the house was observed. The results show that the concentration of the some compounds such as toluene, xylene which are solvents in paint and other finishes was much higher inside the house than outside, just after construction was completed, but decreased rapidly to near the outside level. The total hydrocarbon concentrations behaved similarly. The concentration of chlorinated compounds inside the house were always higher than those outside, but the source of these has not been identified. A concentration distribution model of VOC's based on diffusion has been developed and the parameters of the model are given, based on the determined data.

Introduction

More and more attention has been paid to indoor air pollution recently because the concentration of many pollutants is often higher indoors than outdoors. Identifying the source of the indoor air pollutants, finding the relations between indoor and outdoor air contaminant concentrations and developing models for indoor air pollutant concentration distribution are active subjects of study.

A EPA report[1] indicated that more than 50 volatile organic chemicals, including aromatic hydrocarbons, halogenated hydrocarbons, alcohols, esters, aliphatics and aldehydes are normally found in indoor air and their concentration level is always higher than that outdoors, especially in new buildings. Jarke, et. al.[2] tried to identify the organic contaminants in indoor air and find their relation to outdoor contaminants. They selected about 36 homes in the Chicago metropolitan area, using Chromosorb 102 as adsorbent for GC and GC/MS analysis. 118 compounds were found and identified in indoor air but only 29 compounds were identified in outdoor samples. They concluded that the indoor contaminants probably arise for the most part, from the carpeting, clothing, furniture and the residents' activity in the home. The location of the home relative to industrial operations in the community had a slight effect on the number of contaminants found in the home. Gam-mage and Matthews[3] gave some examples of occupant activities, and consumer and construction products inside residences that cause transient or persistent emissions of volatile organic compounds(VOC) and found that emissions arise from window cleaning, carpet laying, smoking and automobile operations. Montgomery and Kalman [4] used air bag and charcoal tube sampling methods for measurement of some volatile organic compounds at 17 residences in Ruston, Washington and made a comparison of indoor and outdoor air. They showed that indoor air environments were more polluted than the immediate outdoor environments. Johansson [5] investigated the air of two schoolrooms and his results showed that the qualitative composition of indoor and outdoor air is about the same.

This study focuses on a newly constructed and furnished residence. Measurements of both indoor and outdoor air for 12 selected volatile organic compounds were made at random intervals over a 6 month period to observe the concentration distribution beginning as soon as the house was occupied. A model based on molecular diffusion describes the concentration distribution of indoor pollutants.

Experimental

The house chosen for the study is located in a newly constructed townhouse complex near Princeton, NJ. The three story house is heated by gas fueled hot air and has central air conditioning. Gas is also used for cooking. While there is a garage in the first level, it was not used for automobile storage before or during the test period. Most of the floors are carpeted with nylon carpeting and urethane foam padding. The walls are painted with latex paint. Some woodwork has a stain and polyurethane finish.

Samples were taken in the kitchen/dining area on the middle floor of the house. Since the house has a fairly open plan, and forced air heat, this central location could be impacted by pollutants emitted in any area. Outdoor samples were taken simultaneously on a balcony on the second floor, at the front of the house. Since the rest of the complex was mostly incomplete and unoccupied, there was little automobile traffic in the area during the study.

The sampling period was entirely in the cooler months, when ventilation through open windows and doors was minimal. A wood burning fireplace was used 5 times during the period, but not on the same days that sampling was being done. The air conditioning was not used during this time.

Samples were taken by pumping air through Tenax adsorbent at 8 - 10 ml/min for 24 hrs. The traps were analyzed within 2 days. Both indoor and outdoor samples were

taken simultaneously. Sampling began in October 1989 ended in April 1990, and samples were taken randomly with an average of 7 days interval. Samples were taken more frequently in the early stages of the project, when concentrations were changing more rapidly.

The samples were analyzed using a Tekmar 5000 desorption system coupled with a Varian 3700 GC. The sample tubes were desorbed at 250°C for 12 min., and injected into the GC using a -150°C secondary cold trap for focussing the peaks. The column is a 50 meter, 0.3mm I.D. methyl silicone with a 5 μ m film thickness (Hewlett Packard). The effluent is split between FID and ECD detectors. Compounds are identified by retention times, compared with a standard gas mixture containing the target compounds (Alphagaz). Additional samples were run by GC/MS, using a similar column, to verify compound identifies. A blank was done with each day's sample and the minimum detection level was 0.01 ppb for each compound.

Results and Discussion

Figure 1 shows the GC/MS chromatogram of a sample, with the major peaks identified. The total hydrocarbon concentration was obtained by summing all the FID peak areas and using the hexane calibration factor. Figure 2 shows the time distribution of the total hydrocarbon concentration. Initially, there is a very high concentration in indoor air as the construction and finishing materials outgassed. During most of the construction period, the house was well ventilated by open windows, but these were closed for about 2 weeks before sampling began. Within 10 to 15 days, the concentration of indoor hydrocarbons dropped rapidly. After 30 days the concentration became stable and remained fairly constant for the next five months. The total hydrocarbon concentration in the outdoor air remained between 20 and 50 ppb during the six months. This was generally lower than the indoor level. The rapid decrease in the indoor air concentration at beginning indicates that the contaminants are emitted from surface finishes and carpets and are eventually exhausted by diffusion or ventilation, or are adsorbed on interior surfaces. Because of the dead volume inside the house, it is considered that diffusion is the main mass transfer phenomena. Finally, the difference in concentration between indoors and outdoors becomes smaller. The rate of emissions from the various sources becomes equal to the rate of exhaust to the outdoors and a steady state arises.

The concentrations of compounds such as toluene and xylenes, used in paints, showed comparable changes with time. Toluene concentration variation is shown in Figure 3. A similar pattern of concentration is seen in the total hydrocarbons. Benzene and hexane, more volatile compounds, were also like each other, but were different from the heavier compounds. These concentrations decreased more quickly in the indoor air and finally approached that of outdoor air (Figure 4). This may indicate that the lighter compounds are more easily exhausted from emission sources and also are more readily cleared from the indoor air through diffusion. Several C10 hydrocarbon isomers are prominent in the analysis and showed a decline over the course of the project. The source of these was not determined.

The concentration distribution of total chlorinated compounds (i.e. total ECD active compounds) as well as a typical chlorocarbon, 1,1,1-trichloroethane, are shown in Figures 5 and 6. The concentration of these in indoor air was always higher than outdoor, and did not drop during the 6 months. This indicates that the emission source was fairly constant, and did not become depleted. Drycleaned clothing brought into the house may be a contributor, but the actual source has not been identified. Several chlorofluorocarbons of unknown origin were also present at constant levels. Chlorofluorocarbon 113 was the most prominent, with a concentration of about 10 ppb.

The simplest model to describe indoor air concentration distribution based on diffusion and ventilation may be written as:

$$- V \frac{dC_i}{dt} = - R_i + FC_i + D_i A (C_i - C_{O_i}) \quad (1)$$

V : total house volume
 C_i : indoor concentration of compound i
 t : time, hours
 R_i : emission rate of indoor source of compound i
 F : total ventilating flowrate
 D_i : diffusion coefficient of compound i
 A : total diffusion area from indoor to outdoor
 C_{O_i} : outdoor concentration of compound i

During a certain period, if the source and ventilation are considered to make slight contributions, then equation (1) can be rewritten as :

$$- V \frac{dC_i}{dt} = D_i A (C_i - C_{O_i}) \quad (2)$$

$$\text{or} \quad \ln \frac{C_i - C_{O_i}}{C_{O_i} - C_{O_i}} = - \frac{D_i A}{V} t \quad (3)$$

Where C_{O_i} is concentration of compounds i at initial time.

If the emission is significant, and is considered as a diffusion from the source, equation (1) can be rewritten as :

$$- V \frac{dC_i}{dt} = - D_{ei} A_e (C_{ei} - C_i) + D_i A (C_i - C_{O_i}) \quad (4)$$

where D_{ei} , A_e , C_{ei} are the diffusion coefficient, area, and concentration from emitting materials of compound i respectively. Equation (4) is a linear first order differential equation and its solution based on initial conditions $t = 0$, $C_i = C_{O_i}$ is:

$$C_i = a + (C_{O_i} - a) e^{-bt} \quad (5)$$

$$\text{or} \quad \ln \frac{C_i - a}{C_{O_i} - a} = - bt \quad \text{where} \quad (6)$$

$$a = \frac{D_{ei} A_e C_{ei} + D_i A C_{O_i}}{D_{ei} A_e + D_i A} \quad \text{and} \quad b = \frac{D_{ei} A_e + D_i A}{V} \quad (7)$$

From equation (6) it can be seen that, after a period of time, the concentration of indoor contaminants tends to become constant. The concentration is a function of the emission concentration, the diffusion coefficient of the contaminant and the diffusion area of both emission and exhaust. Actually, when the concentration of contaminants in indoor

air is low enough, and the ventilation has little effect on the concentration of contaminants, diffusion can be considered as the main mass transfer path for exhausting contaminants. The plots of the concentration term in equation (3) vs. time for the toluene, xylenes and total hydrocarbon data show the predicted linear behavior early in the sampling, and in later samples, show a different, near zero, slope (Figure 7), indicating early clearance of pollutants by diffusion and later equilibration with surfaces in the residence.

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Fig. 1 GC/MS Analysis of Indoor Air

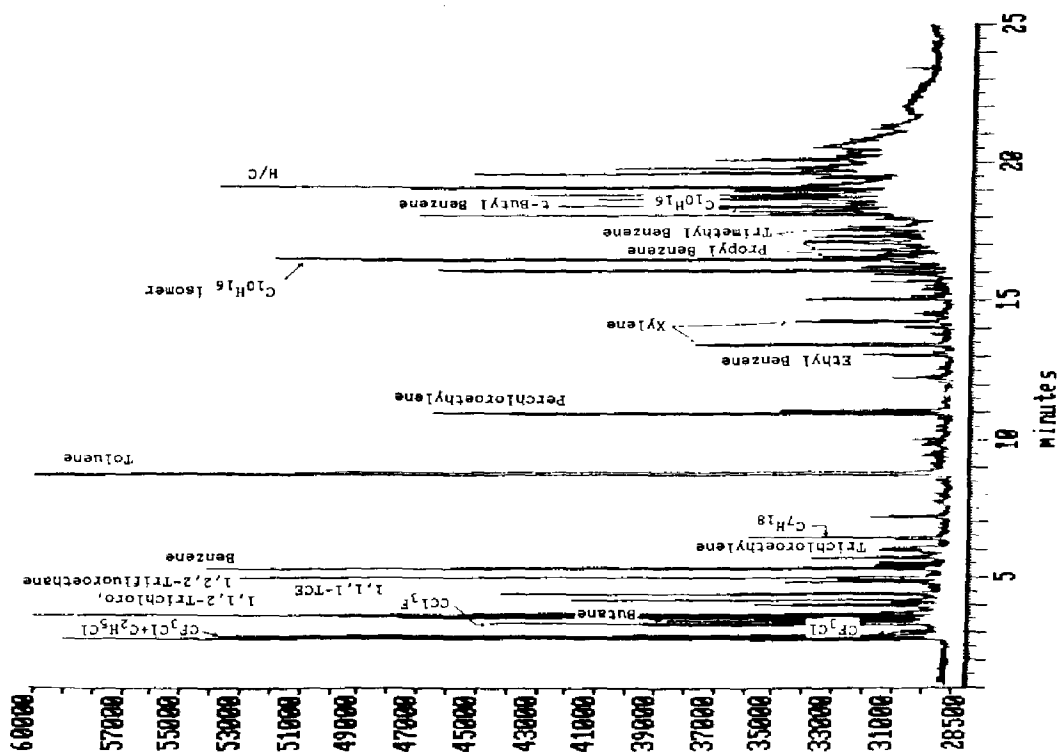


Fig. 2 Total Hydrocarbons

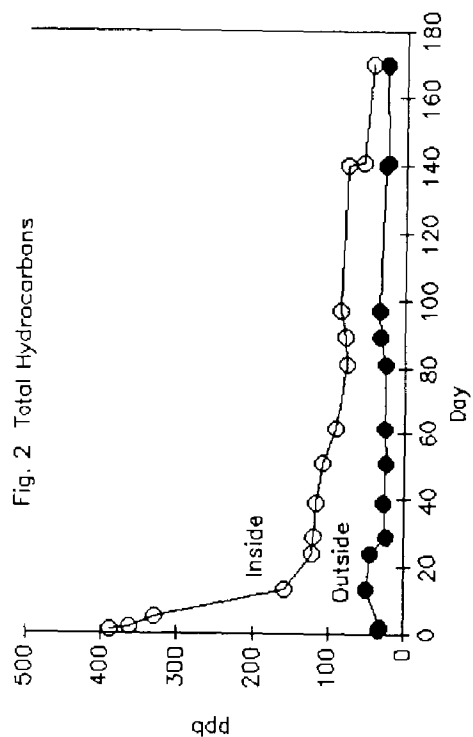
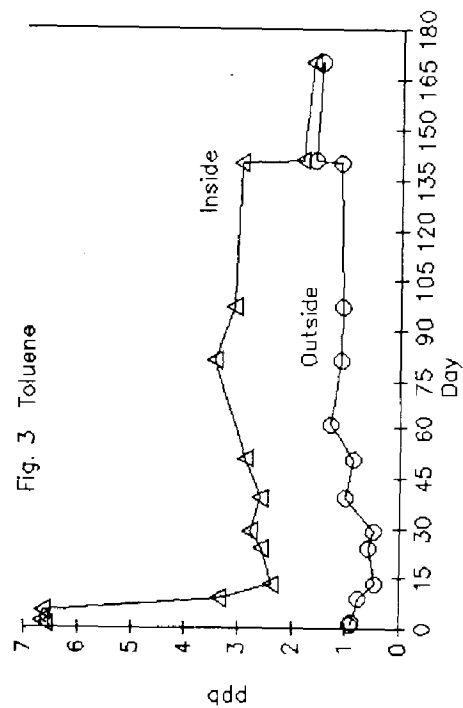
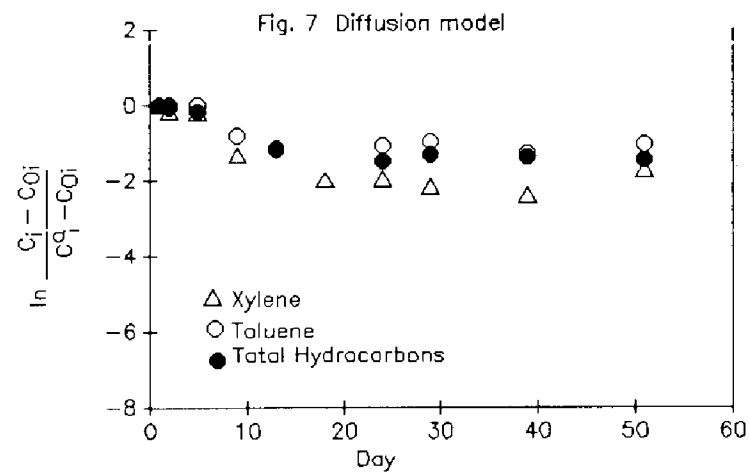
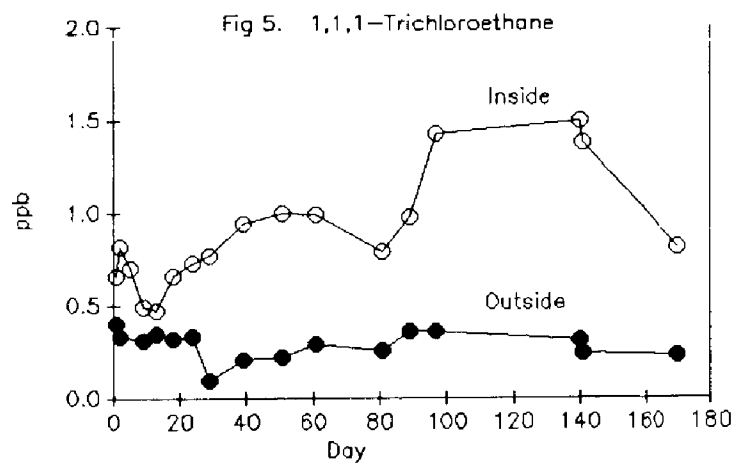
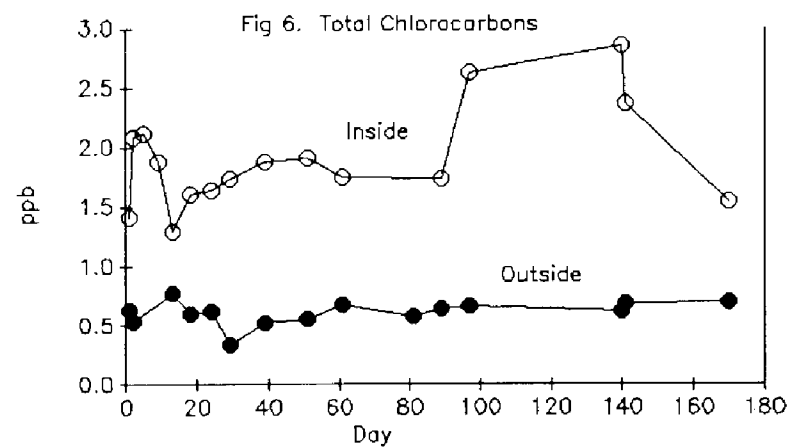
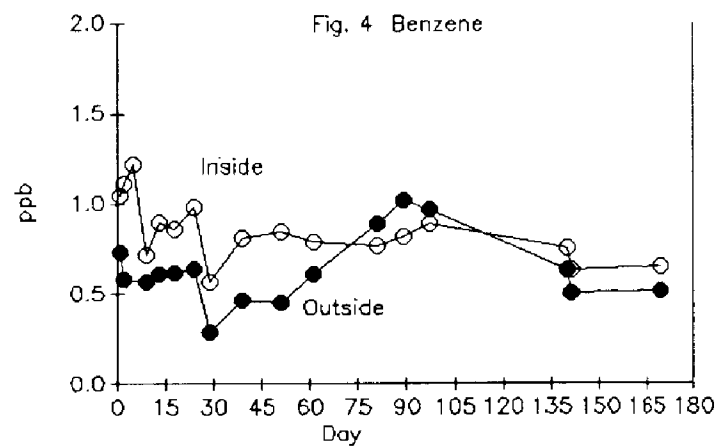


Fig. 3 Toluene





showed that only 45-55% of the total sample was detected. It has previously been demonstrated that PCBs can be extracted quantitatively from PUF². Therefore, something must be interfering with analysis of the extracted analytes. There are two possible explanations to this problem. One possibility is that analytes are being are not being efficiently collected during the cryogenic collection process. The other possibility is that co-eluting interferants (contaminants from the CO₂) are suppressing the ECNI process in the ion source of the mass spectrometer. Many co-eluting impurities are observed in the total ion chromatogram, although we have as of yet been unable to identify these compounds. Levels of freons in SFC grade CO₂ high enough to preclude the use of an ECD for dynamic extractions have been reported by other workers in the field³. Since ECNI responds well to similar classes of compounds as the ECD, it is likely that this is a significant effect. Therefore, it may be necessary to obtain a higher purity grade supercritical fluid for SFE/GC/ECNI/MS experiments, or to spike the PUF with isotopically labeled standards to account for variations in detector response.

CONCLUSIONS

SFE is a rapid alternative to liquid solvent extraction for the removal of semivolatile organic compounds from PUF. SFE can reduce the amount of time needed to perform the extraction step from days to minutes. Coupled SFE-GC analysis should allow sample collection volumes for ambient air to be reduced by two orders of magnitude, and thus decrease sampling time by the same factor. A decrease in sample volume requirements makes small personal sampling pumps useful for collecting samples in locations that otherwise would be inaccessible with a high-volume air sampler (e.g., balloons, remote areas, indoor sites).

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ESTIMATING THE CANCER RISK FROM MULTI-ROUTE EXPOSURE TO CHLOROFORM FROM CHLORINATED WATER

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Abstract

Showers are currently suspected to be as an important source of exposure to chloroform organic as water ingestion. To better estimate the internal chloroform dose from dermal and inhalation exposure from showering, chloroform breath concentration before and five minutes after exposure to chlorinated water was measured. An increase greater than an order of magnitude above the corresponding background breath concentrations was found. The chloroform breath concentration was also determined to decrease exponentially with time following the cessation of the exposure, reaching background levels within two hours. Approximately 30% of the internal dose was expired as chloroform. The calculated internal dose from showering (inhalation plus dermal) was comparable to estimates of the dose from daily water ingestion. The risk associated with a single, ten minute shower was estimated to be 1.2×10^{-4} , while the estimated risk from daily ingestion of tap water ranged from 0.13×10^{-4} to 1.8×10^{-4} for 0.15 and 2.0 liters, respectively. Since the estimates of chloroform risk from domestic water use for the three exposure routes, ingestion, inhalation and dermal are similar, all routes must be used to calculate the total risk when making policy decisions regarding the quality of the municipal water supply.

Introduction

Drinking water regulations for chemical contaminants have been based on the assumption that a daily ingestion of two liters represents the principal source of exposure to chloroform (Interim Primary Drinking Water Regulations). However, showering also exposes individuals to volatile organic compounds (VOC) contained in the water. The exposure from showering is via two routes: inhalation of VOC after transference to air (1,2) and dermal absorption of VOC after water contacts the body (3,4). Chloroform can enter the body via these exposure routes during showering thereby increasing its body burden. Models based on Fisk's law, diffusion considerations and transfer estimates through the skin have indicated that exposure in a shower could yield a similar VOC dose as ingestion (5,6). Since many people take at least one shower each day throughout their lifetime, the potential health risk could be significant. Estimates of chloroform health risks have been extrapolated from high dose animal studies. The partitioning of chloroform among the amount expired, metabolized and absorbed by tissue need to be similar for the extrapolation to be valid. Fry et al. (7) demonstrated that for a 0.5 g dose of chloroform, between 18% and 67% was expired, with amount expired inversely related to body weight. They also found that the majority of the unexpired chloroform was metabolized to carbon dioxide, with little excreted. The objectives of the present study were to: 1) examine the relationship between the chloroform concentration of shower water and breath 2) estimate the percentage of the chloroform internal dose expired at

environmentally relevant levels and 3) estimate chloroform dose and cancer risk from a shower and compare it to that from water ingestion.

Methods

Chloroform exposure and internal dose from showering was estimated from thirteen showers taken by six subjects (5 males and 1 female) using a defined set of parameters. These parameters were either standardized or measured (4). Breath samples were collected from the subject prior to and after each exposure. A water sample was collected along with each shower. The percent of chloroform dose expired was estimated from five series of breath measurements. For three, inhalation only exposure was monitored, and for two, a normal shower was taken. A model shower chamber, constructed of stainless steel, was used to examine inhalation only exposure for durations of 5, 10 and 15 minutes. Breath samples were collected immediately following the exposure, at 30 minutes, one hour and two hours. Breath samples were collected at more frequent intervals following a 10 minute shower for the combine dermal, inhalation exposure. A description of the sampling and analysis for the dose estimates is available in Jo et al (4). The time series samples were collected using a system model after Pellizzari et al (8) and analyzed by thermal desorption/GC/MS.

Estimates of the Expiration of Chloroform

A mathematical model describing the post exposure breath concentration with time was determined by fitting the decay curve to an exponential equation. The equation was integrated to estimate the amount of chloroform expired following the exposure. It was assumed that chloroform was also expired during showering. This was estimated assuming a linear relationship with time.

Estimates of Chloroform Dose from a Shower

The total chloroform dose from a shower was estimated from the sum of the inhalation exposure and dermal exposure. The chloroform dose from inhalation exposure was calculated using the following equation:

$$D_i = E_r \times C_a \times R \times T/W_t \quad (1)$$

where D_i = chloroform dose from an inhalation exposure ($\mu\text{g}/\text{inhalation exposure-kg}$); E_r = respiratory absorption efficiency of chloroform (0.77) (9); C_a = shower air concentration ($\mu\text{g}/\text{m}^3$); R = breathing rate ($0.014 \text{ m}^3/\text{min}$) (10); T = Shower duration (10 min); and W_t = body weight of a reference person (70 kg)

Jo et al. (4) estimated the relative chloroform body burdens for dermal exposure and inhalation exposure from chloroform breath concentrations, while controlling for exposure intensity. The ratio of the body burden resulting from dermal exposure to that from inhalation exposure was 0.93. The chloroform dose from dermal exposure was then estimated from that ratio as follows:

$$D_d = D_i \times F \quad (2)$$

where D_d = chloroform dose from a dermal exposure ($\mu\text{g}/\text{dermal exposure-kg}$); and F = ratio of the body burden from dermal to inhalation exposure (0.93)

Estimates of Chloroform Exposure from Water Ingestion

The chloroform dose from water ingestion was estimated using the following equation:

$$D_{ig} = E_i \times C_w \times A_w/wt \quad (3)$$

where D_{ig} = Dose from water ingestion ($\mu\text{g}/\text{ingestion exposure}\cdot\text{kg}$); E_i = gastrointestinal tract absorption efficiency (100%); C_w = mean tap water concentration ($\mu\text{g}/\text{L}$); and A_w = water amount ingested per day (0.5 and 2 liters/day)

Estimates of Cancer Risk from a Shower and Water Ingestion

The chloroform risk associated with a shower and water ingestion for a reference person was calculated from the estimated doses. A linearized model was used to estimate the cancer potency of the chloroform exposure (11). The model extrapolates animal data at high experimental doses to low environmental exposure levels in order to estimate cancer risk for humans. The cancer risk from a shower was estimated by extending the model developed for ingestion exposure to inhalation and dermal routes of exposure.

$$P_d = q \times D \times 10^{-3} \quad (4)$$

where P_d = lifetime risk; q = cancer risk potency slope ($.26 \text{ mg}/\text{kg}\cdot\text{day})^{-1}$ (11); and D = chloroform dose ($\mu\text{g}/\text{kg}\cdot\text{day}$)

Results and Discussion

Breath analyses confirmed that a chloroform internal dose resulted from both dermal and inhalation exposure during showering. The post-exposure exhaled breath concentrations ranged from 6.0 to 21 $\mu\text{g}/\text{m}^3$. Chloroform was not detected in any breath samples collected prior to a shower. The minimum detection limit (MDL) for the packed GC method for chloroform was 0.86 $\mu\text{g}/\text{m}^3$. Using an estimate of the pre-shower breath concentration as one half the MDL, the chloroform body burden from a shower was 14 to 49 times higher than the background chloroform body burden.

Chloroform was measured in the exhaled breath as a function of time after exposure. The initial study showed a linear increase in breath concentration with exposure duration in a sample collected immediately after an inhalation exposure (figure 1). The pre-exposure breath concentration of three subjects was again less than 0.86 $\mu\text{g}/\text{m}^3$, while the post-exposure, exhaled breath concentrations were 15, 21 and 26 $\mu\text{g}/\text{m}^3$ for 5, 10 and 15 minute exposure durations, respectively. The air concentration in the model shower chamber was estimated to be 160 $\mu\text{g}/\text{m}^3$. It is hypothesized that there is a net absorption of chloroform by the body during showering since the exchange of chloroform between alveolar air and blood across the lung/capillary interface is based on an equilibrium process and the maximum breath concentration was below that in the air being breathed. However, since an equilibrium process exists, some of the previously absorbed chloroform could be expired during showering. The amount expired during shower should be estimatable using the linear relationship shown in figure 1, provided the body is not saturated with chloroform. Once the exposure ceased, the breath concentration declined. The concentrations after one hour were 1.8, 1.5 and 2.4 $\mu\text{g}/\text{m}^3$, for the 5, 10 and 15 minute exposures, respectively, and at or below the detection limit after two hours.

To better define the elimination rate of chloroform, a series of breath samples were collected at frequent intervals following an exposure to chlorinated water. The chloroform breath concentrations measured after exposure to shower water were elevated above the pre-exposure concentrations of <0.4 $\mu\text{g}/\text{m}^3$. The breath concentration was observed to decrease exponentially with time (figure 2). The chloroform breath concentrations

reached background levels within two hours of the end of exposure. An estimate of the amount of chloroform exhaled was made by determining the best fit for the data, assuming that the breath concentration decay with time could be mathematically modelled using an exponential equation. The following equation was derived:

$$C = 2.2 e^{-0.023T} \quad (5)$$

where C is the concentration ($\mu\text{g}/\text{m}^3$) and T is the post exposure time (minutes). Equation 5 was integrated between time equal zero and 120 minutes, the time required for the exhaled breath concentration to the return to the background concentration. The time integrated concentration, $89 \mu\text{g}\cdot\text{min}/\text{m}^3$, was multiplied by the average breathing rate of $0.014 \text{ m}^3/\text{min}$ to determine that a total of $0.99 \mu\text{g}$ of chloroform expired subsequent to exposure. To estimate the amount expired during the shower, the background chloroform breath concentration, $0.4 \mu\text{g}/\text{m}^3$, and the highest breath concentration measured, $3.9 \mu\text{g}/\text{m}^3$, were used as the two endpoints for the ten minute shower exposure. The upper concentration is an underestimation, since the first post-exposure breath concentration was measured more than 2 minutes following the shower and the breath concentration is expected to have decreased during that time interval. The integrated concentration determined, $22 \mu\text{g}\cdot\text{min}/\text{m}^3$, was multiplied by the average breathing rate of $0.014 \text{ m}^3/\text{min}$, to estimate that $0.30 \mu\text{g}$ was exhaled during showering. Thus, an estimated $1.3 \mu\text{g}$ of the chloroform internal dose was expired as chloroform.

The internal dose from showering results from both inhalation and dermal exposures. The inhalation exposure can be estimated from equation 1 using the chloroform air concentration measured during this experiment of $20 \mu\text{g}/\text{m}^3$. Thus the internal dose from inhalation exposure for the individual, who weighed 75 kg, was calculated to be $2.2 \mu\text{g}$. The internal chloroform dose from dermal exposure was calculated using equation 2 to obtain a value of $2.0 \mu\text{g}$. The total internal dose calculated from showering with water containing $20 \mu\text{g}/\text{L}$ chloroform is $4.4 \mu\text{g}$. Therefore 30% of the internal dose was expired. This is within the lower end of the range observed by Fry et al. (10) from an ingestion of 0.5 g of chloroform, an exposure five orders of magnitude larger than in the present study. Their data indicated that the percent expired was inversely related to body weight, an indicator of adipose tissue content. The weight of the subject used in this study was close to the highest weight they reported, thus the subject should have expired a smaller percentage of chloroform than their norm, as was observed. This suggests that the percentage of chloroform expired unchanged, and by inference the amount metabolized, is similar across wide ranges of exposures and supports the validity of extrapolating health effects observed at high chloroform exposures to lower environmental exposures.

To compare the internal chloroform dose from each exposure route, the mean water and air concentrations measure were used. Equation 1 was solved using a shower air concentration of $160 \mu\text{g}/\text{m}^3$ to calculate a chloroform dose from inhalation exposure of $0.24 \mu\text{g}/\text{kg}$. The chloroform dose from dermal exposure, from equation 2 and a water concentration of $23 \mu\text{g}/\text{L}$, was $0.22 \mu\text{g}/\text{kg}$. Thus, the chloroform dose from a shower (inhalation plus dermal) was estimated to be $0.46 \mu\text{g}/\text{kg}$. Using the same water concentration, the estimated daily ingestion dose, calculated from equation 3, was $0.7 \mu\text{g}/\text{kg}$ for a 2 liter water ingestion and $0.05 \mu\text{g}/\text{kg}$ for a 0.15 liter water ingestion. The daily chloroform dose from a shower was between 0.7 and 9 times the dose from water ingestion. The total chloroform dose from a shower was, therefore, equivalent to or larger than the dose from ingestion.

The chloroform risk estimates are summarized by exposure type in Table 1. The risk associated with exposure from a single daily ten minute shower was estimated, from equation 4, to be 1.2×10^{-4} (6.2×10^{-5} for inhalation exposure and 6.0×10^{-5} for dermal exposure), which is comparable to the risk from a daily 2-L water ingestion (1.8×10^{-4}). The risk from a shower was approximately a factor of 10 larger than from ingestion daily of 0.15-L water ingestion (0.13×10^{-4}). If one million people were exposed for a lifetime, the excess cancer risk would be 122 from a single daily 10 minute shower, 180 from a daily 2-L water ingestion, and 13 from a daily 0.15-L water ingestion.

Conclusion

Individuals are exposed to chloroform from daily showers when using chlorine-treated municipal tap water. The chloroform body burden from a shower was estimated to be 14 to 49 times the background chloroform body burden, depending on the shower tap water concentration. The breath concentration rapidly returns to background values within two hours, with approximately 30% of the internal dose expired. Chloroform dose and cancer risk from a single, ten minute shower was equal to or greater than that from daily water ingestion. Hence, in situations where individuals are told not to drink water because it has been contaminated with VOC they should also be told not to shower or bath with the water. Furthermore, the chloroform dose received from showers and from other uses of chlorinated tap water must be considered when agencies and health officials evaluate the quality of a chlorinated water supply.

Acknowledgements

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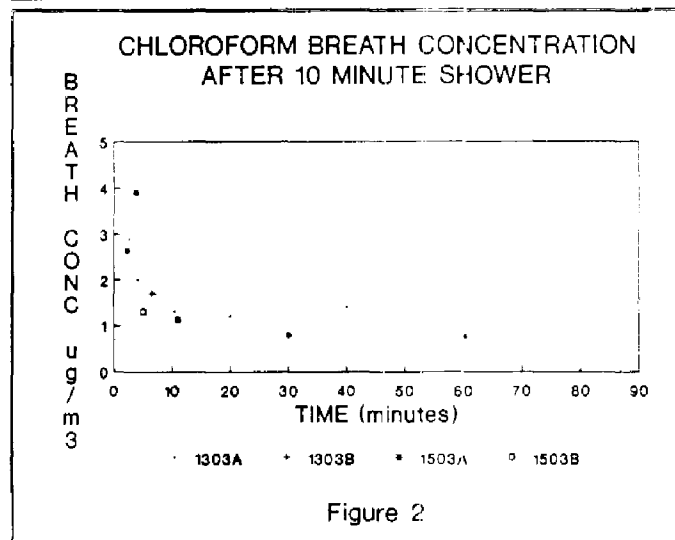
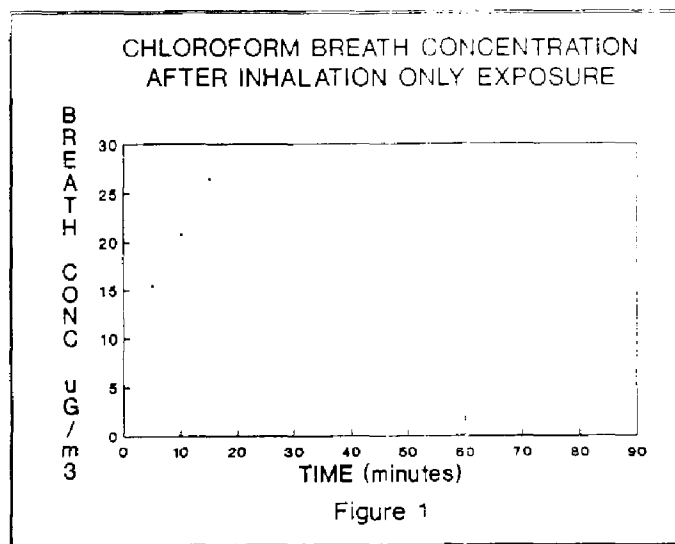
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Table 1 - Chloroform dose and the corresponding risk estimates for the chloroform water concentration of 24.5 $\mu\text{g/L}$

Exposure Type	Dose* ($\mu\text{g/kg-day}$)	Risk (per million)
Normal Shower		
Inhalation Exposure	0.24	62
Dermal Exposure	0.23	60
Total	0.47	122
Water Ingestion		
2-L Ingestion	0.7	180
0.15-L Ingestion	0.05	13

* the dose was estimated based on one shower per day



COMPARISON OF INDOOR AND OUTDOOR ALDEHYDE CONCENTRATIONS DURING THE IACP ROANOKE, VIRGINIA RESIDENTIAL STUDY

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The U.S. EPA's Integrated Air Cancer Project (IACP) conducted a field study in Roanoke, Virginia during November 1988-February 1989. As part of this study, samples were collected in ten pairs of homes, each pair consisting of one home heated by oil and one heated by electricity or gas. Paired homes were located near each other and concurrent sampling was conducted inside each home and outside the one not heated by oil. Average concentrations of the major aldehydes inside homes with and without oil heat were similar and significantly greater than outside levels. A few homes exhibited a diurnal variation of indoor concentrations, but no consistent trends were observed among the homes on a daytime/nighttime, weekend/weekday or day of week basis.

Introduction

Between November 1988 and February 1989, the Integrated Air Cancer Project (IACP) conducted a field study in Roanoke, Virginia. This study was conducted in similar fashion to our previous study in Boise, Idaho during the period November 1986 to February 1987. In the Boise study the focus was on residential wood combustion and mobile sources while the Roanoke study includes residential oil combustion as an additional source. An overview of the Boise study and preliminary results were presented at a previous symposium¹.

The residential phase of the Roanoke study involved ten pairs of homes wherein one home had an oil heating system (IN:WITH) while the other was heated by gas or electricity (IN:W/O). Each week samples were concurrently collected from inside one pair of homes, outside the home without oil heating (OUTSIDE), and at three primary ambient sites. The primary sites included a mobile source site located adjacent to an interstate highway next to Roanoke's Civic Center (CIV), a general residential site located at

Morningside Park (MSP) and a background site located outside the city at Carvins Cove (COV). Samples were collected 7am-7pm and 7pm-7am every day at the primary sites and on Saturday through Tuesday at the residential sites to observe daytime vs. nighttime and weekend vs. weekday variations.

Experimental Methods

Aldehydes were collected on dinitrophenylhydrazine (DNPH) coated silica gel cartridges² in duplicate (collocated). All sample flow rates were maintained using mass flow controllers. The DNPH derivatives of carbonyl species were eluted from the sampling cartridges with 5 mL of acetonitrile and analyzed by high performance liquid chromatography (HPLC). Two C-18 columns (25 cm x 4.6 mm) in series were employed using an acetonitrile/water gradient and detection at 360 nm. Aldehyde identities were determined by retention time comparison with standards.

Results

The collocated samples were analyzed for about one half of the sampling periods of the residential study. The percent difference between ppb concentrations for the collocated samples averaged 2.85% for formaldehyde and 10.39% for acetaldehyde (indicating a contamination problem with acetaldehyde). Review of all field blanks revealed consistently low formaldehyde levels, while acetaldehyde levels varied in a random fashion with no correlation relative to sampling site or storage time between cartridge preparation and analysis. Comparison of blank cartridges stored at RTP, NC with those stored in Roanoke (and not taken out to sampling sites) showed elevated levels of acetaldehyde for the Roanoke samples. This indicated some of the contamination observed in the blanks may have occurred in Roanoke during storage or during transportation to and from RTP. Problems with acetaldehyde blanks or contamination has not been evident in previous IACP field studies or numerous other studies where we have employed the cartridge technique. The source of contamination is still under investigation. Because the contamination is of a random nature and blanks do not exist for every sampling period, the data presented here have not been corrected for the blank background. Based on a typical sample, the average acetaldehyde contamination is equivalent to 1.73 ppb (v/v). Acetone contamination was also evident, but this is typical due its ubiquitous nature.

Table I gives the average aldehyde concentrations observed during the residential study. Formaldehyde, acetaldehyde, and acetone account for about 90% of all the carbonyls measured. Except for a trivial difference for o-tolualdehyde, the average indoor concentrations are always greater than outside and indoor concentrations show little sensitivity to the type of heating employed. The problem with contamination from acetaldehyde and acetone is readily apparent from the measurements made outside the homes, i.e. the acetone concentration is 4 times greater than formaldehyde and the formaldehyde/acetaldehyde ratio is 1.1. Formaldehyde/acetaldehyde ratios of 2 are more typical which suggests the actual outdoor concentration of acetaldehyde may be about 1.1 ppb. In our previous IACP field study conducted in Boise, Idaho, the outside formaldehyde/acetaldehyde average ratio was 1.85 based on individual samples and average concentrations of formaldehyde and acetaldehyde were 4.40 and 2.38 ppb respectively³. Note that the average ambient formaldehyde concentrations observed in Boise are about twice those of Roanoke. Average formaldehyde concentrations inside Boise homes without wood stoves (16.3 ppb) were similar to the homes in Roanoke without oil heating (16.9 ppb). Average formaldehyde concentrations inside homes with wood stoves in Boise (22.2 ppb) however, were higher than

those inside Roanoke homes either with or without oil heating.

Figure 1 shows the average formaldehyde concentrations observed for the residential samples in Roanoke relative to daytime and nighttime while Figure 2 shows average concentrations (daytime + nighttime) for each day of the week. In all cases, no significant trends were observed. Figure 3 shows the average concentrations of formaldehyde, acetaldehyde and acetone for all ambient sites sampled in Roanoke for the Saturday-Tuesday period. Concentrations are similar for the residential outside (RES) and residential park (MSP) samples while the mobile source site (CIV) is slightly elevated. The background site (COV) shows reduced formaldehyde but is similar to the residential samples with respect to acetaldehyde and acetone, again indicating the contamination problem with these species.

The formaldehyde levels observed for each sampling period inside and outside the homes without oil heating are shown in Figures 4 and 5, respectively. Mean concentrations are shown by the solid line while the dotted and dashed lines represent plus and minus one or two standard deviations, respectively. The first block in each group represents Saturday-daytime followed by Saturday-nighttime etc., the last block being Tuesday-nighttime. While an occasional day>night pattern is evident, e.g. week 9, there is no consistent pattern at the various homes studied. There is no correlation between cooking and or frying in the homes and the concentration of formaldehyde (and other aldehydes such as hexanaldehyde and acrolein) found. This may relate to the fairly long 12-hour sampling time relative to these activities and the effects being averaged over adjacent sampling periods. On the other hand, these activities may only be minor contributors to the overall concentrations observed.

In the indoor and outdoor data plots, one statistically significant outlier is evident, i.e. week 4 for the outside samples and week 7 for the indoor samples. Outdoor samples were collected via a glass manifold located inside a trailer parked adjacent to the home without oil heating. Outside air was continuously pulled through the manifold and a portion of this air pulled through a smaller manifold where the outdoor cartridge samples were collected. A small leak in any of the connections between the glass manifold and the cartridges could result in contamination by air inside the trailer. The indoor samples had the cartridges located inside the home with all sampling pumps, etc. located in the trailer downstream of the cartridges. Any leaks in this system might result in reduced flow through the cartridges, but would not be a source of contamination. We have observed indoor concentrations similar to week 7 in previous studies and have no valid reason to reject these samples. Outdoor concentrations and air exchange rates appear to have little influence on observed indoor formaldehyde concentrations.⁴ Personal activities, home construction and furnishings appear to be the main variables which influence indoor concentrations. The outdoor concentrations observed for week 4 appear unrealistic and are harder to explain. (Mean values reported in Table I do not include these samples.) While the observed levels could be a result of some local point source, there is some indication that these outdoor samples may have been contaminated with indoor air due to a leak in the sampling system. For week 4, the outdoor samples have formaldehyde concentrations slightly greater than their corresponding indoor levels. Hexanaldehyde concentrations were also elevated relative to the indoor samples. In the Boise study, we did have a few elevated outdoor formaldehyde samples, but did not also see corresponding higher levels of minor species such as hexanaldehyde. We currently consider the week 4 samples atypical and will compare the aldehyde data to other gas phase samples, e.g. organic hydrocarbons, when that data becomes available.

Conclusions

Average concentrations of most carbonyls were higher inside homes than outside with formaldehyde concentrations being 7 times higher indoors than outdoors. The indoor formaldehyde concentrations were similar in all the homes with one exception and no correlation with heating systems, i.e., oil burners or gas and electric was found. In general, aldehyde concentrations indoors did not exhibit consistent diurnal or day of week trends. Activities of individuals, furnishings, etc. are likely the major factors affecting carbonyl concentrations in homes. Correlation of cooking activities with observed indoor aldehyde levels was not consistent. Contamination of field samples with acetaldehyde was observed, the causes of which are still being investigated.

Disclaimer

The research described in this paper has been reviewed by the Atmospheric Research and Exposure Assessment Laboratory, US EPA and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Agency nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

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Table 1

Recovery of organochlorine pesticides from PUF
using supercritical CO₂

<u>COMPOUND</u>	<u>MW</u>	<u>% RECOVERY^a</u>	<u>SD</u>
HCB	282	96.5	3.2
Heptachlor	370	113.1	5.0
Heptachlor Epoxide	386	99.8	2.3
Oxychlordane	420	99.6	3.2
<u>gamma</u> -Chlordane	406	111.6	6.8
<u>alpha</u> -Chlordane	406	106.8	3.2
<u>trans</u> -Nonachlor	440	106.5	9.0
p,p'-DDE	316	108.9	7.5
Dieldrin	378	105.5	5.0
Endrin	378	97.9	8.2

^aAverage of three extractions. The PUF plug was ca. 1 cm in diameter and 2.5 cm long

Table I. IACP Roanoke residential study average aldehyde concentrations, ppb(v/v).

COMPOUND	OUTSIDE ^a	IN:WITH	IN:W/O
Formaldehyde	2.26	15.68	16.87
Acetone	9.51	12.86	12.57
Acetaldehyde	1.91	9.16	9.60
Unknowns	0.63	1.31	1.45
Hexanaldehyde	0.03	1.21	1.09
Propanaldehyde	0.20	1.02	0.85
Butyraldehyde + MEK ^b	0.27	0.45	0.64
Valeraldehyde	0.02	0.48	0.43
Acrolein	0.11	0.50	0.38
Benzaldehyde	0.05	0.38	0.38
p-Tolualdehyde	0.01	0.11	0.11
Iso-valeraldehyde	0.00	0.08	0.07
Crotonaldehyde	0.02	0.09	0.06
m-Tolualdehyde	0.00	0.03	0.02
o-Tolualdehyde	0.01	0.00	0.00
Total w/o acetone	5.72	30.51	31.95
Total carbonyls	15.03	43.38	44.52

a. Does not include data from week 4.
b. MEK = methylethylketone.

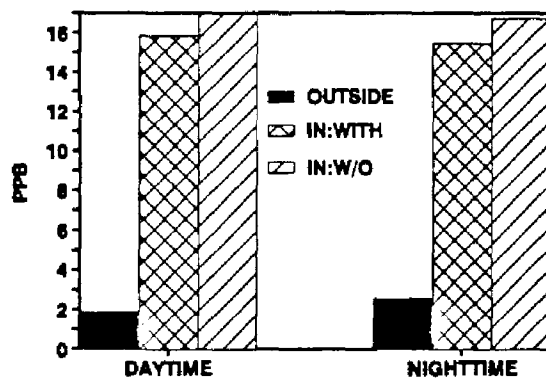


Figure 1. Average formaldehyde concentrations observed at residential sites during daytime and nighttime.

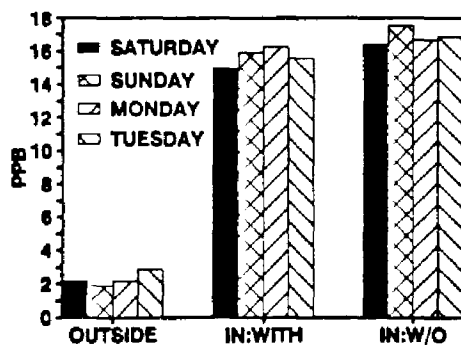


Figure 2. Average indoor and outdoor concentrations of formaldehyde observed by day of the week.

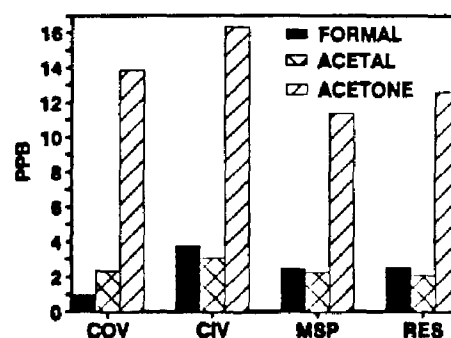


Figure 3. Average ambient concentrations of major carbonyls observed at residential and primary sites.

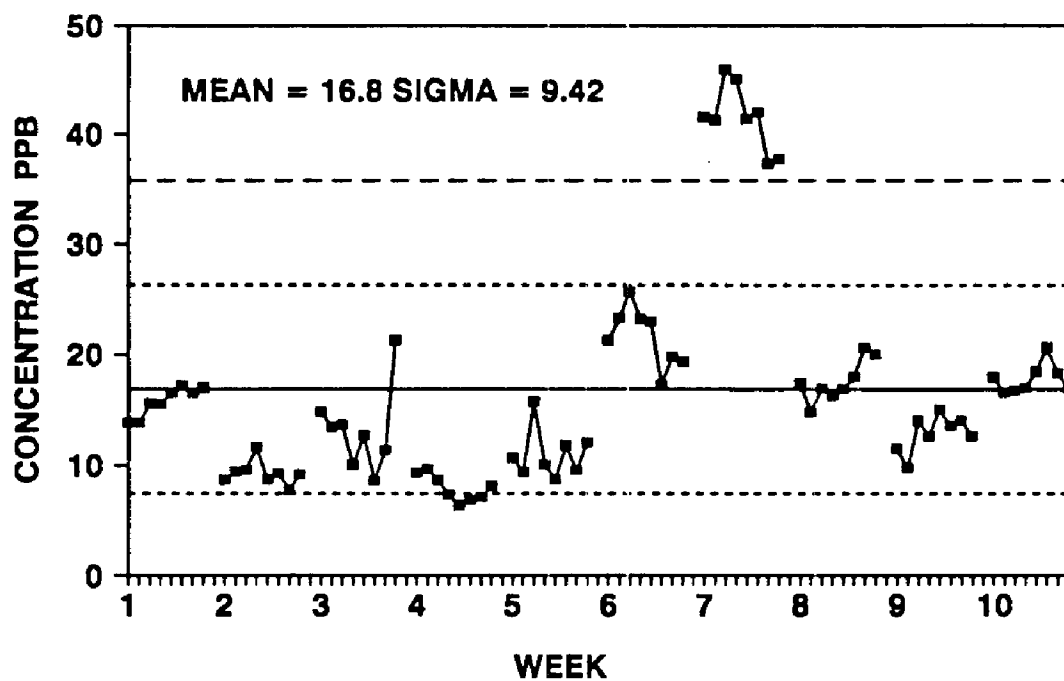


Figure 4. Formaldehyde concentrations observed for each sampling period at homes without oil heating.

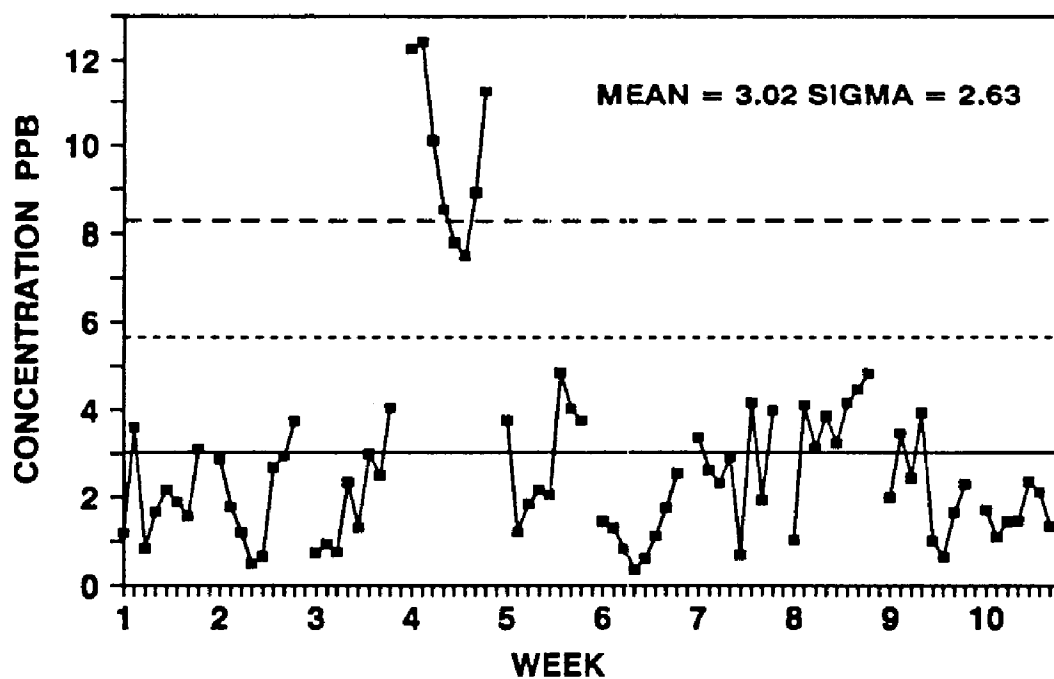


Figure 5. Formaldehyde concentrations observed for each sampling period outside homes without oil heating.

RISK CHARACTERIZATION OF NONCANCER HEALTH EFFECTS ASSOCIATED WITH INDOOR AIR POLLUTANTS

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To date, risk characterization efforts associated with indoor air pollutants have primarily focused on carcinogenic risks. While cancer risks are an important concern, experience to date has shown that, related to indoor air pollutants, noncancer health effects may be more widespread and significantly affect the work environment, worker health and performance. Sick Building Syndrome (SBS) has become a common problem attributed to volatile organic compounds (VOC), biological contaminants and other pollutants. SBS symptoms are noncancer in nature, emphasizing the importance of noncancer health effects from indoor air pollution. Very little work has been carried out in characterizing noncancer risks. Most effort has focused on defining acceptable daily intakes or Reference Doses (RfD) rather than estimating incidence and severity of the wide range of effects within an exposed population. There are several significant differences between risk characterization for cancer and noncancer health effects. These differences have significant bearing on the manner in which indoor air pollutants should be measured and exposures characterized.

INTRODUCTION

The objectives of this paper are to review the nature of characterizing noncancer health effects, identify implications of this risk characterization on indoor air pollutant data and measurements, attempt a risk characterization for an example complex mixture of indoor air pollutants, assess the quality of available data on indoor air pollutants, and identify future research needs.

NATURE OF RISK CHARACTERIZATION OF NONCANCER HEALTH EFFECTS

Noncancer effects are assumed to have thresholds, and vary widely, typically having multiple endpoints, multiple target organs and multiple symptoms of varying intensity and severity. Coupled with the thresholds concept is the issue as to what constitutes an "adverse health effect".

The severity of effects vary greatly from a physiological response with no apparent effects in an individual as a whole, to a clinical response or disease, and finally to disability and/or death. "Adverse" effects are defined as any effects which result in functional impairment and/or pathological lesions which may affect the performance of the whole organism, or which reduce an organism's ability to respond to an additional challenge.¹

At low exposure concentrations, a homeostatic state occurs in which the organism has the ability to adapt to a minor insult with no change in overall physiology, no physical effect is observed, though psychological or subjective changes may be perceived by an individual. As concentration or dose increases, a compensatory state is reached where functional impairment and subtle effects which are not adverse may occur without loss of overall integrity of the organism through some defense mechanism such as metabolic detoxification. As exposure or dose further increases, small portions of the populations exhibit adverse frank effects, where the dose has exceeded the body's compensatory or defense limits and organ and system function is impaired, disease may be apparent. When dose is increased the incidence of adverse effects will increase, as will the severity of the effect observed. At some point, the entire population would exhibit an adverse response, though there would be a distribution of severity of effects. The goal of noncancer risk characterization is to define the distribution of effects and severity of these effects within the population for the organ systems affected.

The complexity of characterizing noncancer health effects is exemplified by a condition commonly associated with indoor air exposures, Sick Building Syndrome (SBS), a common problem consisting of acute, nonspecific sensory irritation and other sensory effects. The World Health Organization (1983)² defined SBS symptoms to include (1) eye, nose, and throat irritation, (2) sensation of dry mucous membranes, (3) erythema (skin irritation, redness), (4) mental fatigue and headaches, (5) high frequency of airway infections and cough, (6) hoarseness and wheezing, (7) itching and unspecific hypersensitivity, and (8) nausea and dizziness. The variety of endpoints is apparent in this condition, affecting multiple organs (eye, respiratory etc...) with varying severity (eye irritation to unspecific hypersensitivity).

IMPLICATIONS ON RISK CHARACTERIZATION

This multi-dimensional nature of noncancer health effects has implications on all components of the risk characterization process. As stated above, the goal is to define the distribution of effects within a population for several organ systems for various levels of severity. Each of the organ systems would have a threshold for each of the adverse effects. Thresholds are both time and concentration dependant, as concentration increases response time is decreased. Appearance of noncancer effects may be immediate or delayed, and either permanent or transient. To characterize effects, most efforts to date have focused on the use of thresholds for effects from long-term exposures and to define protective exposure levels (i.e., RfD) for such exposures rather than specific dose-response functions. In theory, thresholds could be determined for a range of effects for specific exposure patterns such as acute, short-term and long-term exposures, not just for long duration exposures. However, even the simplified approach of using thresholds presents problems for risk characterization. Average lifetime exposures are inadequate for comparison to acute and short-term thresholds. Greater detail is required in defining dose, exposure, and pollutant concentration. Peak and cumulative values, in addition to an overall average, are required for comparison to the

appropriate threshold levels. This is especially important considering most indoor pollutant exposures are transient with varying concentration.

Individual exposures in the indoor environment are heavily influenced by the time individuals spend in particular microenvironments and the activities they are engaged in while in those microenvironments. The timing of an exposure is important when concentrations are variable over time, as in the decay profile of offgassing from new building materials. Likewise, activities are important in that it may result in very high transient exposures (e.g., the use of consumer cleaning products) or affect dosimetric factors (e.g., increased breathing rate associated with physical activity) which may increase the effective dose.

Each microenvironment has its own concentration profile, peak, and average concentration. Actual overall exposures are the aggregation of all individual microenvironment exposures. An overall average exposure level, aggregated over all microenvironments, does not allow for comparison of peak exposures, from individual microenvironments, to relevant thresholds. Therefore greater detail is needed in characterizing pollutant concentration and time activity patterns for several common microenvironments.

APPLICATION TO AN EXAMPLE COMPLEX MIXTURE

Table 1 presents an example complex mixture of VOCs identified as major pollutants in a problem building. Employees experienced increased health complaints following building renovations which included painting and installation of carpets and office partitions. Sampling of the work environment indicated a typical indoor air quality problem, multiple compounds at low concentrations. Actual ambient sampling data were limited and inconsistent, for both constituents and their concentrations.

The data in Table 1 are from direct sampling and model estimates. The first seven compounds were identified as major constituents in carpet offgas. The values are from samples taken from new carpet of the same batch stored in a warehouse. As offgassing emissions from new products tend to decay with time, these measurements are assumed to be maximum exposure levels. The remaining three compounds have been associated with office partitions and other materials using particleboard. The expected ambient concentration estimates of the three compounds attributed to office partitions as a source were calculated based on chamber studies to characterize emissions rates, and a model which considers environmental and ventilation conditions.³ The values in the table are assumed to be worst-case (at 0.1 air changes per hour, ACH). These 10 compounds and their respective concentrations will be used to attempt a risk characterization for this complex mixture.

IDENTIFICATION OF HEALTH EFFECTS

Initial efforts focused on identifying the possible health effects associated with the compounds identified in Table 1. A search was made in the College of Medicine's database, TOXNET, for each of the compounds in the following fields: human toxicity excerpts; populations at special risk; absorption, distribution, and excretion; metabolism/metabolites; biological half-life; mechanisms of action; interactions; and threshold limit values (TLV). Only noncancer health effects which have been reported for humans were recorded and summarized for the following organ/systems, eyes, nose, respiratory, central nervous system, blood, skin, as well as a miscellaneous category. As an example, the summary matrix for the central nervous system is presented in Table 2. The designation of an X within a cell

TABLE 1. VOLATILE ORGANICS FOUND IN EXAMPLE COMPLEX MIXTURE

<u>Compound</u>	<u>Concentration (ppb)*</u>	<u>Method</u>	<u>Value</u>
Toluene	13.0 - 22.0	GC/MS, GC/FID	Peak
Ethylbenzene	3.7 - 4.6	GC/MS, GC/FID	Peak
Xylene	4.6 - 8.6	GC/MS, GC/FID	Peak
Styrene	31.0 - 33.0	GC/MS, GC/FID	Peak
Cumene	4.1 - 6.9	GC/MS, GC/FID	Peak
4-Phenylcyclohexene	70.7**	GC/MS, GC/FID	Peak
Dichlorobenzene	18.0 - 68.0	GC/MS, GC/FID	Peak
Formaldehyde	61.0***	Chamber, Model	Worst-case
Acetaldehyde	15.0***	Chamber, Model	Worst-case
Acetone	55.0***	Chamber, Model	Worst-case

* Range of concentrations represent the values from GC/FID and GC/MS. Measurements made on new stored materials and are assumed to represent the maximum exposure levels.

** 4-PCH concentration from GC/FID, presence confirmed but no concentration quantified on GC/MS.

*** Predicted concentrations at 0.1 ACH due to other building materials (office partitions) using a model developed by the EPA, Air and Energy Engineering Research Laboratory (AEERL).

Source: *USEPA, Internal memo from Burchette and Singhvi to T. Fields, dated 5/22/88.

***USEPA, Internal memo from Tichenor to D. Weitzman dated 8/25/88

indicates that effect has been reported in humans for a given compound. An asterick by the effect listing indicates that that particular effect was reported in the problem building. The information in the Table is not exhaustive, but illustrative of the range of possible effects due to a particular compound. The absense of an X does not imply the effect is not possible, only that it has not been reported in TOXNET. This method is qualitative and limited by the availability of toxicological or epidemiological data for specific compounds. It should also be noted that the exposures for which effects were reported in TOXNET were typically occupational, at exposures significantly higher than that found in the indoor environment. While limited, this method is useful in identifying the range of probable effects and in identifying particular compounds of concern.

To introduce a quantitative element to the risk characterization, the observed concentrations were compared to two common thresholds, Threshold Limit Values (TLV) and odor thresholds. The TLV is intended for use in occupational settings and is not intended for application to the general public. However, it is an easily recognized standard that is widely used to establish indoor and outdoor exposure limits and does provide a gross appraisal of possible health effects. Odor thresholds may play an important role in indoor air quality problems. Some hypothesize that odors may be either bringing attention to otherwise ignored symptoms, association of the source of odors as the source of the symptoms, or leading to symptoms directly.⁴ TLVs and odor thresholds have been found for all compounds except 4-phenylcyclohexene (4-PC) for which only an odor threshold has been defined. These are presented in Table 3. Observed concentrations were several orders of magnitude lower than their respective TLVs, and odor

Table 2: SUMMARY OF REPORTED NONCANCER HEALTH EFFECTS DUE TO INDOOR AIR POLLUTANTS COMPRISING THE MIXTURE

EFFECT	COMPOUND								
	<u>AcA</u>	<u>ACE</u>	<u>CUM</u>	<u>DCB</u>	<u>EtB</u>	<u>FOR</u>	<u>STY</u>	<u>TOL</u>	<u>XYL</u>
<u>CENTRAL NERVOUS SYSTEM</u>									
Tinnitus								x	
Headache				x			x	x	
* Dizziness		x	x	x				x	
* Depression							x		
* Fatigue							x		
* Confusion							x	x	x
Drowsiness	x		x						
Vertigo		x	x	x			x		
Slowed Reaction Time		x							x
Intoxication: Euphoria			x						
Exhilaration		x						x	x
Boastful., talkative		x							
Incoordination (ataxia)		x	x				x		x
* Anesthesia							x	x	
Edema							x		
Weakness		x		x			x		
* Effects Reprted Associated With The Example Complex Mixture									

* Effects Reprted Associated With The Example Complex Mixture

thresholds were exceeded for three compounds, acetaldehyde, formaldehyde, and 4-PC. This approach can be expanded to any effect which has an identified threshold.

The efforts described above have focused on assessing the toxicity of individual compounds. Indoor air exposures are typically mixtures, as in the example complex mixture, so it is desirable to develop some method to assess the toxicity of a mixture rather than just for the individual

Table 3: COMPARISON OF OBSERVED CONCENTRATIONS TO TWO EXAMPLE THRESHOLDS

	Maximum	TLV (ppm)	Odor Threshold*(ppm)
	Obs. Conc. (ppm)		
Acetaldehyde	0.015	100	0.00011 - 2.3
Acetone	0.055	750	19.675 - 668
Cumene	0.0069	50	0.008 - 1.3
Dichlorobenzene	0.068	75	2.0 - 30
Ethylbenzene	0.0046	100	2.0 - 200
Formaldehyde	0.061	1	0.05 - 49
Styrene	0.033	500	0.047 - 200
Toluene	0.022	100	2.14 - 70
Xylene	0.0086	100	0.08 - 40
4-Phenylcyclohexene	0.072	--	0.001 - 0.01**

* Source: Ruth, 1986.⁵

** Source: Unpublished reports

components. Based on a review of suggested EPA approaches⁶ and others proposed in the literature, an approach of using mixture index values has been applied. Several options for these mixture index values have been identified and include: (1) Hazard Index, (2) Margin of Exposure, (3) Additivity (with Relative Potency), (4) Response Addition, (5) Comparative Potency and Toxicity Equivalent Factors, (6) Total Organics (or by Chemical Class), (7) Indicator Compound Concentrations, (8) Interactions, and (9) Tiered Approach.

The hazard index, margin of exposure, and additivity assume additivity of effects, and involve the summation of health effects for individual compounds. Comparative potency is different in that the toxicity of the mixture is assessed directly without attention to individual components. Comparative potency is based on the assumption that animal bioassays are applicable to human health prediction and mixtures are compared based on bioassay results.⁷ The total chemical class approach assumes little difference in relative potencies between compounds with the same chemical characteristics. The indicator compound approach assumes that a single compound is indicative or responsible for a large fraction of total health effects. Interactions is a formal approach for addressing the physiological effects individual compounds have on one another, either synergistically or antagonistically. The tiered approach integrates elements of previous approaches. It would have a ceiling threshold to protect against a severe (clinical) effect, and a dose-response component to estimate the distribution of less severe effects at concentrations below the ceiling threshold.

Two mixture index value approaches have been applied to the example complex mixture, the hazard index (HI) and margin of exposure (MOE). These indexes and their application to the complex mixture (for those constituents with EPA verified inhalation RfDs) are described in Table 4. MOE_is have been calculated for these compounds and are all within an order of magnitude of each other, and are several orders of magnitude lower than their individual no observed adverse effects level (NOAEL). For a mixture, the MOE is sum of the MOE_i for the individual constituents for a given target organ. Individual MOE_i should only be summed for the same target organ system. A MOE_i for the central nervous system (MOE_{CNS}) was calculated summing the MOE_is for the 3 compounds having a NOAEL for the central nervous system. The MOE_{CNS} was calculated as 0.00443. This is interpreted as the exposures are about 0.4% of the "threshold value for the mixture".

The hazard index approach is the most commonly applied method for noncancer effects from mixtures.⁶ Values exceeding 1 indicate that the RfD has been exceeded. The HI_i values calculated for those 5 compounds having verified inhalation RfDs vary from 0.032 for toluene to 3.056 for cumene. This is interpreted as toluene exposure is at about 3% of the RfD, while cumene exposures are more than 3 times the RfD level. Cumene exposures are predicted to exceed the RfD. However, before any conclusions are made it should be noted that cumene has a high uncertainty factor (10,000) and a low confidence designation. Therefore in reviewing the mixture and relative importance of each constituent and in the overall index value these factors should be considered.

An overall mixture Hazard Index was calculated for the central nervous system (HI_{CNS}). The value of 3.184 indicates that the exposure is more than 3 times the estimated "mixture RfD". However, it should be noted that the cumene which, as described above, has the highest uncertainty and lowest confidence designation, contributes about 96% to the overall index value. Therefore this uncertainty should be included in any interpretation of this index value. While there is significant uncertainty in the RfD, this is the

only method which predicts or substantiates some health (CNS) effects for the example mixture.

CONCLUSIONS

In reviewing the application to the example complex mixture it can be concluded that the data are preliminary and limited, with compounds and effects identified. The data have been shown to be adequate in defining peak pollutant concentration levels and for subsequent comparison to some threshold values. However, existing data are inadequate to define actual exposures and dose and subsequent use of dose-response relationships. Existing data was also inadequate in that only 5 of the 10 compounds had verified inhalation RfDs which limited the use of the mixture index approaches. Concentration profiles were also nonexistent prohibiting the calculation of actual exposures and dose. It was not known if all compounds were present at their respective maximum concentrations simultaneously. It is also not known whether the sampling taken from the stored virgin material actually represents the peak concentration, actual peak may be higher to increased emissions due to increased surfaces area exposed. To apply the mixture index values, concentration profiles for each chemical in the mixture should be used for the same time period. Exposure to peak concentrations different chemicals at the same time versus different times will give different index values.

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TABLE 4. INDEX APPROACH EXAMPLES

Compound (i)	(ppb) Obs. Conc.	(ppb) NOAEL	Study Species	Organ/Effect	(MOE) _i	UF	mg/m ³ ^{RfD}	ppb	Conf. ¹	HI _i
Acetaldehyde	15.0	66,000 (LOAEL)	Rats	Histopathological changes in resp. tract	0.00227	3,000	0.04	22	M/L/L	0.682
Cumene	5.5	18,700 (LOAEL)	Rats	CNS, nasal irritation	0.00294	10,000	0.009	1.8	L/L/L	3.056
1,4-Dichlorobenzene	43.0	11,210	Rats	Urinary protein output incr. liver, kidney wts.	0.00384	100	0.7	115	H/M/M	0.374
Toluene	17.0	40,000	Human	CNS (Dizz. headache) eye, nose irrit.	0.000425	100	2.0	533	M/M/M	0.032
Xylene	6.6	6,200	Human	CNS, irritation	0.00106	100	0.3	69	M/M/M	0.096

Margin of Exposure (MOE)

$$MOE_i = \text{Obs. Conc.} / \text{NOAEL}$$

$$\text{e.g. } MOE_{\text{CNS}} = \sum MOE_i$$

$$MOE_{\text{CNS}} = MOE_{\text{CUM}} + MOE_{\text{TOL}} + MOE_{\text{XYL}}$$

$$= (0.00294) + (0.000425) + (0.00106)$$

$$(MOE)_{\text{CNS}} = 0.00443$$

-> 0.4% of observed threshold level

Hazard Index (HI)

$$HI_i = \text{Obs. Conc.} / \text{RfD} \\ (\text{where RfD} = \text{NOAEL} / \text{UF})$$

$$\text{e.g. } HI_{\text{CNS}} = \sum HI_i$$

$$HI_{\text{CNS}} = HI_{\text{CUM}} + HI_{\text{TOL}} + HI_{\text{XYL}}$$

$$= 3.056 + 0.032 + 0.096$$

$$HI_{\text{CNS}} = 3.184 \gg 1$$

¹Confidence: Study/Data Base/RfD

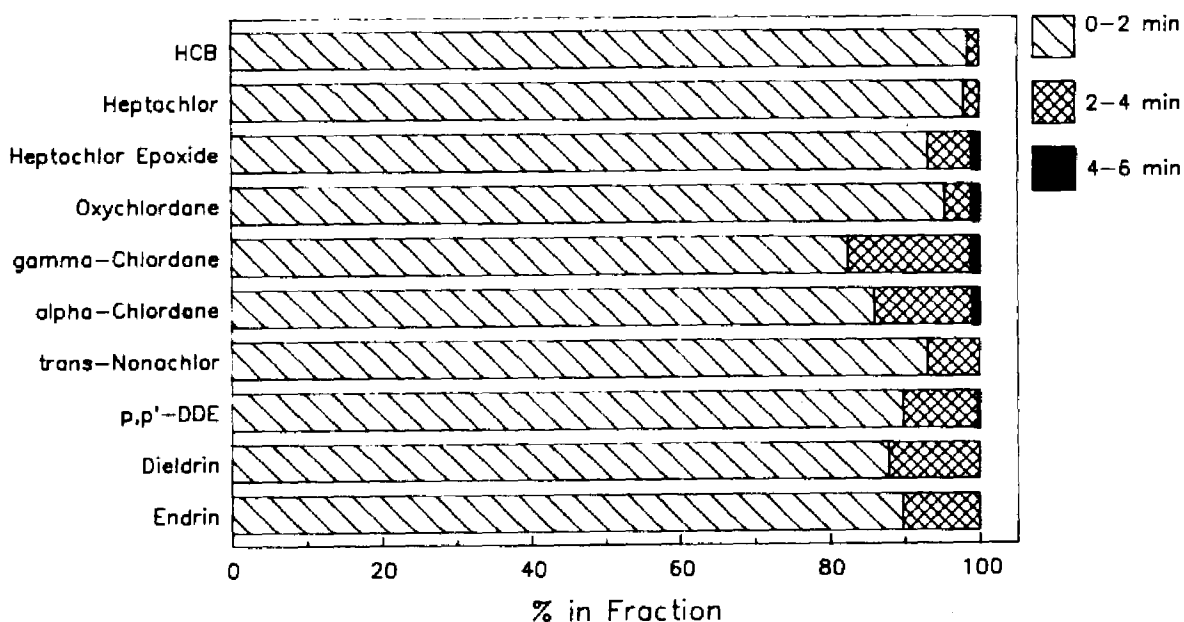
H = High
M = Medium
L = Low

Figure 1

Recovery vs Time

300 atm CO₂

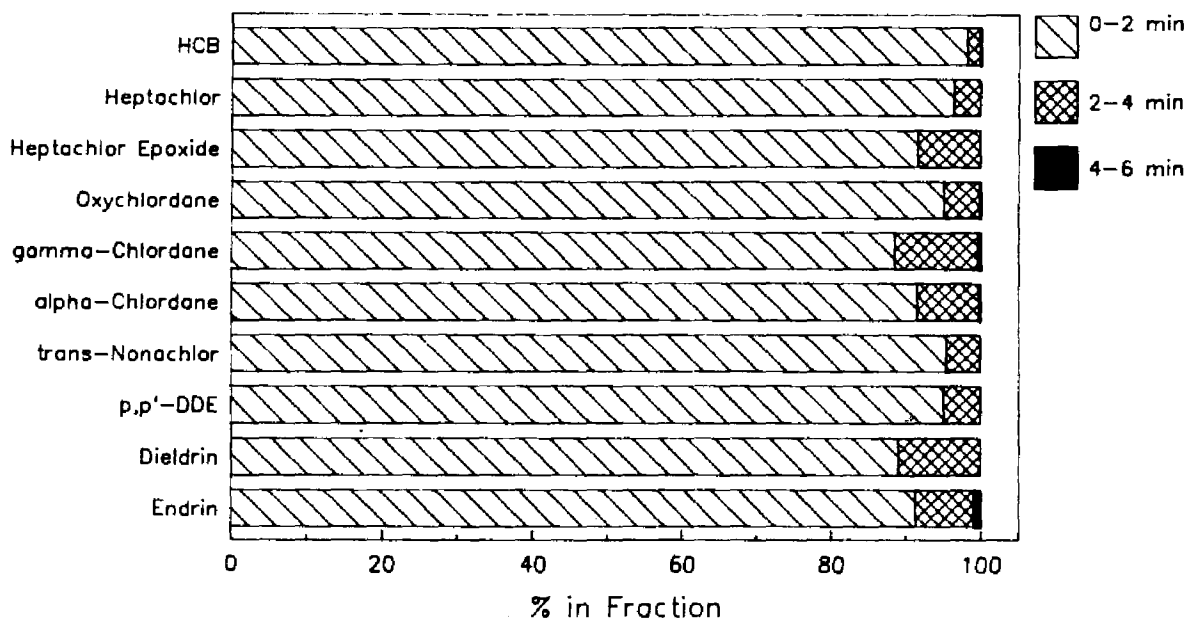
50 C



Recovery vs Time

300 atm N₂O

50 C



Percent recovery vs time for several organochlorine pesticides. The 6-8 minute and 8-10 minute fractions showed no detectable traces of any of the analytes.

ASSESSMENT OF THE HEALTH RISKS ASSOCIATED WITH
INDOOR BENZENE VAPOR EMITTED FROM BUILDING
FOUNDATION SOIL: A CASE STUDY

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Abstract

Benzene is often the main chemical of concern associated with gasoline residues in soil. Occupants of buildings constructed on gasoline-contaminated soil may be exposed to significant indoor air concentrations of benzene vapor emitted from soils underlying building foundations. This paper describes a screening-level approach for evaluating the potential hazards associated with inhalation of indoor benzene vapor emitted from building foundation soil. A combination of two predictive models is used to derive an upper-bound estimate of the airborne benzene concentration inside a structure built on gasoline-contaminated soil. First, the benzene vapor flux from the soil is estimated using the known or estimated soil benzene concentration and Farmer's steady-state model. The benzene concentration inside the building is then estimated using a simple diffusion-ventilation or "stirred-tank" model. The variables used in this model are the benzene generation rate in indoor air and the building's ventilation rate. The benzene generation rate is the product of the predicted benzene flux and the total area of openings in the foundation that allow entry of gaseous benzene into the building. The minimum ventilation rate is estimated using building code requirements. Uptake of benzene by building occupants and the attendant theoretical excess cancer risk is estimated using standard factors for exposure and risk prediction. Predictive modeling approaches such as those used in this assessment are useful tools for conducting screening level health risk assessments when cost or time constraints preclude the measurement of vapor flux and/or airborne chemical concentrations.

Introduction

The leakage of volatile liquids from underground storage tanks is a significant environmental problem. Because many substances stored in these tanks contain chemicals considered to be hazardous to human health, leaks draw concern from the public and environmental regulatory agencies. However, the occurrence of a chemical spill or leak alone is not enough to pose a health threat to the public. An accurate evaluation of the potential for an underground tank leak to actually pose a significant health threat to the public involves an assessment of the magnitude and extent of the contamination, the toxicological properties of the agents, and the potential degree of human exposure. Environmental regulatory agencies often require that a risk assessment be conducted in order to ensure that no threat to public health exists or will exist as a consequence of environmental contamination, such as that produced by an underground tank leak or spill.

In this paper, an underground gasoline spill that occurred in Southern California was evaluated. A developer wanted to build a "fast food" restaurant on the site having gasoline contaminated soil. There was a concern regarding the possibility for the chemicals to migrate through the soil and the building foundation, contaminating the air inside the restaurant. Inhalation of vapors is the only pathway of exposure considered since no human contact with the soil or groundwater is expected to occur. For the sake of simplicity, benzene is the only chemical considered in this example, however, the screening risk assessment methodology presented herein can be applied to other chemicals, with the appropriate consideration of their volatilities (diffusion coefficients) and potencies. The approach employed here can also be applied to similar spills at other sites, with the careful consideration of differing site-specific information.

Due to time constraints and the relatively low levels of volatile organic compounds (VOCs) detected in the soil, a screening-level assessment of the potential health risks associated with inhalation of benzene vapor is deemed to be sufficient for initial evaluation. The screening methodology involved using the combination of two predictive models: one for estimating the benzene vapor flux from the contaminated soil, and one for estimating the attendant airborne benzene concentrations inside the restaurant. The latter prediction involves the use of several assumptions regarding the potential for chemical vapor to penetrate building foundations and the ventilation standards for commercial structures. Finally, estimates of carcinogenic health risks associated with exposure to the estimated indoor airborne benzene concentrations are calculated using standard factors for exposure and risk prediction.

Experimental Methods

Modeling Benzene Vapor Emissions

Although direct measurement of vapor flux from area sources contaminated with volatile organic compounds (VOCs) is possible they are not always feasible or cost-effective. However, predictive models are available for estimating gas emission rates from areas contaminated by losses of VOCs from spills, leaky underground storage tanks, pipelines or surface impoundments.

Such predictive models are useful when project cost or time constraints preclude direct measurement of vapor flux, or when rough "upper-bound" estimates of flux are sufficient.

Farmer's model is used to predict the benzene vapor flux from the gasoline-contaminated area. This mathematical model is based on vapor-phase diffusion, as described by Fick's First Law of molecular diffusion. Vapor phase diffusion is the dominant mechanism for the transport of volatile, low solubility chemicals through the vadose (unsaturated) zone. The model was developed for estimating chemical emission rates from covered landfills without internal gas generation. It was validated in a laboratory using industrial landfill soil contaminated with hexachlorobenzene. The model is used to predict the movement and steady-state vapor loss rates of chemicals from landfills. The predicted non-decreasing emission rate is generally an overestimate because it disregards decreases in soil contaminant concentrations due to volatilization, leaching, and/or biodegradation. Farmer's equation is as follows (Farmer, 1980):

$$F = \frac{(D)(P_A^{10/3}/P_{TOT}^2)(C_G - C_o)}{L}$$

where:

- F = Vapor flux from the soil surface (mg/sec-cm²),
- D = Vapor diffusion coefficient in air at 25°C (cm²/sec),
- P_A = Volumetric air content of soil (cm³_{air}/cm³_{soil}),
- P_{TOT} = Total soil porosity (cm³_{air + water}/cm³_{soil}),
- = 1 - (b/p)
- where:
- b = Dry soil bulk density (g_{dry soil}/cm³_{soil}); and
- p = Soil particle density (assumed to be 2.65 g/cm³).
- C_G = Concentration of chemical in soil vapor below cover (mg/cm³_{air}),
- C_o = Concentration of chemical at soil surface. (mg/cm³_{air}). Assumed to be zero.
- L = Thickness of clean soil cover (cm).

Estimating Benzene Concentration in Soil Vapor

In order to employ Farmer's model in estimating the benzene vapor flux from soil, the concentration of benzene in the soil vapor must be determined. An approach to estimating the chemical concentration in the soil vapor given its total concentration in soil is suggested by Jury et. al. (Jury et. al, 1983), and is utilized in this report. Jury's approach is based on the fact that the chemical resides in a combination of the vapor, liquid, and solid, or adsorbed, phase, and it focuses on determining how a given quantity of chemical will partition between these three phases. Jury uses Henry's law for liquid-vapor partitioning and a linear equilibrium sorption isotherm for solid-liquid partitioning. The following equation relates the total chemical concentration in the soil to its vapor phase component:

$$C_G = C_T / R_G$$

where:

- C_G = Chemical concentration in vapor phase (mg_{chem}/cm³_{air})
- C_T = Total chemical concentration in soil (mg_{chem}/cm³_{soil})

R_G = Gas partitioning coefficient that gives ratio of chemical concentration in vapor phase to total concentration ($\text{cm}^3_{\text{air}}/\text{cm}^3_{\text{soil}}$)
 = $bK_D/K_H + P_L/K_H + P_A$
 where:
 b = Dry soil bulk density ($\text{g}_{\text{dry soil}}/\text{cm}^3_{\text{soil}}$),
 K_D = Slope of the chemical's adsorption isotherm of the distribution coefficient (ml/g)
 = $(F_{oc})(K_{oc})$
 where:
 F_{oc} = Fraction of organic carbon in the soil
 K_{oc} = Chemical's organic carbon distribution coefficient (ml/g)
 K_H = Chemical's dimensionless Henry's Law constant ($\text{cm}^3_{\text{liquid}}/\text{cm}^3_{\text{air}}$)
 P_L = Volumetric moisture content of soil ($\text{cm}^3_{\text{liquid}}/\text{cm}^3_{\text{soil}}$)
 P_A = Volumetric air content of soil ($\text{cm}^3_{\text{air}}/\text{cm}^3_{\text{soil}}$)

Predicting Airborne Benzene Concentration in Indoor Air

The indoor benzene concentration under transient conditions may be approximated by the following mass balance relationship:

the rate of change of the mass = generation rate - removal rate
 of benzene in indoor air

This relationship is represented mathematically by the following differential equation:

$$\frac{d(Vc)}{dt} = G - Qc$$

where:

V = Volume of building (m^3)
 c = Indoor air concentration of contaminant (mg/m^3)
 t = Time (hours)
 G = Generation rate of chemical in indoor air (mg/sec)
 = $F \times A$

where:

F = Benzene vapor flux predicted by Farmer's model ($\text{mg}/\text{sec}-\text{cm}^2$)
 A = Total area of openings in building foundation (cm^2)
 Q = Ventilation rate in building (m^3/sec)

The above differential equation can be solved for $c(t)$ to obtain:

$c(t) = (G - G e^{-Qt/V}) / Q$, which, at steady state, reduces to $c = G/Q$.

To estimate the generation rate of benzene in indoor air, it was assumed that the amount of benzene vapor which will diffuse through the building foundation concrete is negligible in comparison with the benzene vapor which will enter the building through openings in the foundation. This assumption is based on a study by Zapalac (1983) in which he showed that this was true for radon diffusion through concrete. The benzene generation rate in indoor air, then, is simply the product of the benzene vapor flux predicted using Farmer's model and the aggregate area of all openings in the building foundation (e.g. cracks, floor-wall joints, loose

fitting pipes, weeping tiles). The average California home has 2-10 cm² of openings per m² of floor area, and the values in this range are greater than the estimated leakage area for commercial buildings (Grimsrud et al., 1983). Therefore, this assessment uses the lower limit of the range for homes in California, 2 cm² per m² of floor space.

The ventilation rate for the proposed restaurant was assumed to be 7 ft³/min per person inhabiting the building. This rate is suggested as a minimum ventilation rate by the American Society of Heating, Refrigerating, and Air-Conditioning Engineers (ASHRAE) for fast food restaurants in which smoking is not permitted. If smoking is allowed, a 5-fold increase in the ventilation rate is required. These ASHRAE standards are used in the building codes of 45 states in the U.S. (ASHRAE, 1981). The proposed restaurant will have an occupancy of 14 persons, resulting in a minimum ventilation rate of 98 ft³/min or 0.046 m³/sec.

Estimating Carcinogenic Risk Associated with Inhalation of Benzene

The incremental lifetime cancer risk associated with exposure to airborne benzene vapor inside the proposed restaurant is estimated using the following equation:

$$\text{RISK} = \text{Indoor Air Concentration } (\mu\text{g}/\text{m}^3) \times \text{Unit Risk Value } (\mu\text{g}/\text{m}^3)^{-1}$$

The Unit Risk Value (URV) for inhalation is a chemical-specific value derived from the chemical's inhalation potency factor. The URV is defined as the risk posed by inhalation of air containing 1 $\mu\text{g}/\text{m}^3$ of the chemical. It assumes a breathing rate of 20 m³/day, a body weight of 70 kg, and a lifetime of constant exposure. Since no one is expected to spend their entire lifetime in a restaurant, this approach adds another layer of health-conservatism to this screening-level assessment.

Results

Based on soil characteristics measured at the site and chemical-specific parameters for benzene, the flux of benzene vapor from soil was predicted to be 2.9×10^{-8} mg/sec-cm², using Farmer's model. Based on this upper-bound flux estimate, and the fact that the floor area of the restaurant will be 74 m², the generation rate of benzene vapor in the indoor air of the restaurant is calculated as follows:

$$\begin{aligned} c &= \text{FA/Q} = 2.9 \times 10^{-8} \text{ mg/sec-cm}^2 \times 74 \text{ m}^2 \times 2 \text{ cm}^2/\text{m}^2 / 0.046 \text{ m}^3/\text{sec} \\ &= 9.3 \times 10^{-5} \text{ mg}/\text{m}^3 = 0.093 \mu\text{g}/\text{m}^3 \end{aligned}$$

The inhalation URV for benzene is $8.3 \times 10^{-6} (\mu\text{g}/\text{m}^3)^{-1}$ (SHEAS, 1989), which results in a incremental lifetime cancer risk of 7.7×10^{-7} or 7.7 in 10 million.

Conclusions

In this screening analysis, an upper-bound for the potential cancer risk posed by indoor benzene vapor emitted from gasoline-contaminated soil underlying a proposed restaurant was evaluated. Because the building in this case study had not been built yet at the time the risk assessment was

required by a regulatory agency, a predictive method was used to estimate the worst-case indoor airborne benzene concentration. The indoor benzene concentration was based on the benzene emission rate from the soil underlying the building foundation, which, due to time and cost constraints, was also estimated using a predictive tool. The estimated vapor flux from soil was also an upper-bound prediction.

Predictive models such as the ones used in this study are very useful tools for the risk assessor, because cost and/or time constraints often preclude the measurement of chemical concentrations in environmental media. Also, some chemicals may pose a health threat at levels which are not detectable using currently available monitoring procedures, so predictive modeling may be the most feasible way to evaluate the potential for environmental contamination to threaten public health.

The incremental lifetime cancer risk associated with exposure to the benzene vapor inside the restaurant was calculated using standard inhalation exposure assumptions and a risk prediction factor for benzene suggested by the EPA. The calculated risk is certainly an upper bound for the potential incremental cancer risk posed by benzene emissions from the gasoline-contaminated soil. The carcinogenic risk estimate was 7.7 increased cancer risks for every 10 million people exposed to the benzene vapor. Any risk lower than 1 in 1 million is traditionally considered to be an insignificant risk by environmental regulatory agencies (Young, 1987).

This assessment is a screening analysis that is likely to greatly overestimate the actual levels of human exposure. Its purpose is to determine whether the site warrants additional study to more accurately estimate the true risks. Since the calculated risk level was so low, it is clear that a more detailed analysis is not necessary. In summary, this analysis shows that modeling can be a useful tool in screening assessments of contaminated soil.

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A REVIEW OF THE ACCURACY AND PRECISION OF THE TOXIC AIR
CONTAMINANT MONITORING PROGRAM OF THE CALIFORNIA AIR RESOURCES
BOARD

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The California Air Resources Board (CARB) operates a 20 site air monitoring network to measure ambient levels of toxic air contaminants (TAC). The network has been in operation since 1985. Gaseous samples are collected over a 24-hour period using a low volume gas sampler designed by CARB. The samples are transported to the laboratory for analysis. Several routine checks are used to assess the accuracy and precision of this system, and to ensure that data of the highest possible quality are produced. The results of several quantitative measures used to assess the quality of the data are presented in this paper.

In 1988, the CARB staff initiated a performance audit program which is designed to test the accuracy and precision of the overall sampling and analysis system for gaseous TACs. The audit procedure involves introducing an audit sample directly into the intake probe of the sampler. Results for the most recent year of these "through-the-probe" audits show that, on average, the monitoring system is unbiased for 8 of 9 compounds. Several individual audit results are in error by up to 70%, although the majority (70%) of the results are within $\pm 20\%$. The average precision for all compounds is $\pm 40\%$. The individual estimates of precision for 6 of 7 compounds compare well with the precision estimates derived from ambient collocated data.

Introduction

The California Air Resources Board's (CARB) monitoring network for gaseous toxic air contaminants (TAC) consists of 20 sites where 24-hour samples are collected twice each month¹. Samples are collected using a low volume sampler designed by CARB. From 1985 through 1989, Tedlar bags were used as the collection media. Beginning in 1990, 6 liter Summa polished canisters are used to collect samples. Samples are transported to the laboratory for analysis of 10 compounds. In 1988, a "through-the-probe" audit system was implemented to test the accuracy and precision of the entire gaseous TAC sampling, transportation and analysis procedure. The audits are conducted annually at each of the sites in the TAC monitoring network. The results of through-the-probe audits yield information regarding the quality of the ambient TAC data produced.

Configuration and Operation of the Audit System

The through-the-probe audit system (Figure 1) consists of a pure air source (Aadco 737 pure air generator plus a methane reactor), a gas cylinder containing Research Triangle Institute (RTI) certified concentrations of TACs, and a dilution system (a modified Dasibi 1009 MC). The dilution air generated by the pure air source has been analyzed by GC/MS and GC/ECD-PID and is well within CARB's laboratory criteria for clean air acceptability. The Dasibi 1009 MC was modified by replacing all sample lines and fittings with cleaned stainless steel parts, removing the large mixing chambers and enclosing the mass flow controllers in an insulated chamber with a heater to minimize potential wall effects. The mass flow controllers are certified every three months against a National Institute of Standards and Technology (NIST) traceable primary flow standard. The development of the through-the-probe audit method is described in more detail elsewhere².

The output of the dilution system is directed to the inlet of the low volume toxics sampler (Xontech Model 910) for a 24-hour period. The sample is collected and transported to the laboratory for analysis in the same manner as an ambient sample³. The audits are performed on routine TAC sampling dates, so the laboratory is not aware that the sample is an audit until after the analysis is completed.

Most of the through-the-probe audit data available to date is from audit samples collected in Tedlar bags. CARB is currently in the process of switching to 6 liter canisters as the collection media for TAC samples. Several audits have been conducted at sites which have initiated canister sampling, but currently there are insufficient data to characterize canister samples. Results for audits using canisters are not included in this paper.

Nine of the ten compounds monitored are included in the audit cylinder. They are methylene chloride (DCM), chloroform (CHCl₃), carbon tetrachloride (CCl₄), ethylene dichloride (EDC), 1,1,1-trichloroethane (TCEA), ethylene dibromide (EDB),

trichloroethene (TCE), perchloroethylene (Perc) and benzene. Although ambient TAC samples are analyzed for 1,3-butadiene, this compound is not included in the TAC cylinder currently used for through-the-probe audits.

Limitations and Assumptions of the Audit Procedure

The gas cylinder used for the through-the-probe audits can be diluted to a wide range of air to gas ratios. However, the relative concentration of the TACs is the same for each audit. Additionally, the audit cylinder is a pure mixture of the nine compounds listed above. Therefore the audits do not account for matrix effects which may affect ambient data. When the audit results are used to represent the quality of ambient data, it is assumed that the ambient matrix does not substantially affect the TAC results.

Another assumption essential to an analysis of the audit results is that each site is indistinguishable from any other site regarding the monitoring equipment and the way it is operated. Since the goal of the program is to audit each site annually, only one or two audits are currently available for each site. The assumption makes it possible to group the individual results into the same population. It is a reasonable assumption since precautions have been taken to ensure that common equipment is used and a common protocol is followed at each site.

Summary of Results From 1989 - 1990 Audits

Although CARB has used the through-the-probe audit procedure since 1988, only results from 1989 and 1990 audits are presented here. Beginning in 1989, the laboratory has used ambient concentration standards produced by NIST. All of the results presented in this paper were obtained using these high quality laboratory standards.

Results for 12 to 15 individual audits were averaged to obtain mean bias for each compound. These data are presented in Table I. The sample mean bias is statistically significantly different than zero for one compound, methylene chloride (DCM), at the 95% level of significance. However, a regression analysis of DCM observed audit values versus expected values shows that the slope of the linear relationship is not significantly different than 1.0, and the y-intercept is not significantly different than zero. This suggests that the bias, although statistically significant, is small compared to the variability of individual data points.

The 95% confidence intervals for the true mean bias for each compound are shown graphically in Figure 2. Only one compound, DCM, has a mean bias that is significantly different than zero. The 95% prediction intervals for individual results are also shown. While the prediction intervals show that individual results may be in error by up to 75% (eg. EDC and TCEA), on average there is no bias in the results for 8 of the 9 compounds. This suggests that imprecision rather than bias is responsible for the inaccuracy of individual results.

QUANTITATIVE EXTRACTION AND ANALYSIS OF ENVIRONMENTAL SOLIDS USING SUPERCRITICAL FLUID EXTRACTION (SFE) AND SFE-GC

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Supercritical fluid extraction (SFE) reduces the time needed for the extraction and recovery of environmental pollutants from sorbent resins, air particulates, and soils and sediments to 5-30 minutes compared to several hours required by conventional liquid solvent extraction methods. SFE essentially eliminates the generation of waste solvents, as well as the need for concentration steps. When SFE is directly coupled to capillary GC (SFE-GC), sample collection, extraction, analyte concentration, and gas chromatographic separation can be completed in a total time of < 1 hour. The use of SFE and SFE-GC for the rapid and quantitative determination of organic air, water, and soil pollutants including PAHs, heteroatom-containing PAHs, PCBs, wood smoke phenolics, fuel components, and ionic surfactants will be discussed. Quantitative claims for SFE and SFE-GC are supported by the analysis of NIST certified standard reference materials (air and diesel particulates and marine sediment), multiple extractions, and spike recoveries.

Determination of Trends and Outliers

Figures 3 through 11 show individual audit results in chronological order. The two lines above and below zero bias are data screening lines. These lines are determined by calculating two relative standard deviations (2RSD) using valid audit results which represent normal operating conditions. The lines are not straight because they represent a moving 2RSD, ie. points on the data screening lines are recalculated after each audit result.

The chronological plots can be used to identify trends and unusual events. If an audit result exceeds the data screening lines, or if a trend of increasing or decreasing audit results occurs, the sampling and analysis procedures are investigated. If no problems are detected, the result is included in the calculation of the data screening lines and used to determine if future data points are unusual. If a problem is detected, corrective action is taken. Although the audit result is valid, it is not used in calculating the data screening lines because it is not representative of normal conditions. In some cases, the problem is in the audit procedure itself, and the audit results are considered invalid.

Several data points or groups of data which exceed the data screening lines can be seen in Figures 3 through 11. In most cases when these audit results were investigated, no problems were found. Therefore, in most cases the results were included in the calculation of subsequent points on the data screening lines. There were, however, two specific examples of unusual results which led to the discovery of an unsuspected problem.

When the TCEA result for audit 89-17 (Figure 7) was investigated, the laboratory discovered an instrument malfunction which affected TCEA only. The malfunction caused negative biases in the three subsequent audits as well, therefore these results were not included in the calculation of the data screening lines. As a result of this discovery, all routine sample analyses were shifted to a second instrument until the problem was solved. Ambient TCEA data for samples analyzed with the malfunctioning instrument were deleted from the database.

EDB results for audits 89-10 through 89-13 (Figure 8) show a trend of increasing bias. Upon investigation, it was determined that the EDB concentration in the laboratory standard was decreasing. Therefore these three audit results were not included in the calculation of the data screening lines. As of November 1989, a new standard was purchased and assigned for EDB based on the NIST primary standard.

Calculation of Method Variability

If a sufficient number (10 to 15) of through-the-probe audits have been performed, the results can be used to estimate total system method variability. This estimate of total system method variability can be compared to the

estimate obtained using collocated sampling data for each compound where both data sets are available. Method variability (defined as $\pm 2\text{RSD}$) for each compound is presented in Table II.

Three of the 20 sites in CARB's TAC network have collocated (duplicate) gaseous samplers. Method variability can be estimated from collocated data using the following equation.

$$\text{Method variability} = (2 * s / \text{avg. conc.}) * 100$$

where s is estimated by⁴

$$s = [(\text{sum of differences})^2 / 2 * k]^{1/2}$$

where k = number of data pairs

Data from all three sites were combined to obtain estimates of method variability. It is assumed that there are no important differences between sites. It is also assumed that these three sites are representative of the other 17 sites in the network. Because each site has similar monitoring equipment and is operated according to the same protocol, these are reasonable assumptions.

Total system variability estimates using the two estimation methods are comparable for 6 of 7 compounds. The collocated method variability estimate for TCE is significantly higher than the through-the-probe estimate. This may be due to the lower average concentration of TCE (0.17 ppb) detected in ambient air as compared to the average audit concentration (1.0 ppb). Two compounds, EDC and EDB, are consistently lower than the detection limit in ambient air. Therefore no collocated method variability estimate is available. Since 1,3-butadiene is not contained in the audit cylinder, a through-the-probe estimate of method variability is not available.

Future Plans for the Through-the-Probe Audit Procedure

The current through-the-probe audit system is designed to dilute a single audit cylinder. Although the cylinder can be diluted to a wide range of ratios, the relative concentrations of the compounds are always the same for that audit cylinder. CARB is currently developing a modified dilution system which will dilute up to three cylinders to different ratios. The result will be more flexibility in the relative concentrations of the audit gas mixture. Additionally, this system will allow CARB to perform audits using NIST standards which are similar to the laboratory NIST standards but at higher concentrations. Due to gas stability issues, the NIST certified compounds are contained in four separate cylinders. The use of these standards for through-the-probe audits has been limited because the current system can dilute only one cylinder at a time; therefore only a few compounds could be audited at one time.

Conclusions

CARB's through-the-probe audit system has been in operation for two years. The most recent data, collected in 1989 and early 1990, show that CARB's TAC monitoring network is unbiased for 8 of 9 compounds. The exception, methylene chloride, is biased by an average of + 12%. The variability of the audit results is representative of the variability of routine ambient data for 6 of 7 compounds. The average variability for all compounds is $\pm 40\%$ at the audit concentrations of TACs. These results suggest that the potential inaccuracy of any individual data point is due primarily to variability in the sampling and analysis system, rather than bias.

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Table I.

Mean Bias and Standard Deviation for Through-the-Probe Audits
January 1989 - February 1990

Compound	n	Mean Bias (%)	SD Bias (%)	p value	Significant at alpha=0.05?
DCM	15	11.9	15.9	0.01	yes
CHC13	15	3.4	20.6	0.54	no
CC14	15	1.3	12.5	0.70	no
EDC	14	0.2	34.7	0.99	no
TCEA	12	-5.2	32.3	0.56	no
EDB	13	-4.3	15.6	0.34	no
TCE	15	-2.9	10.9	0.32	no
Perc	15	6.4	14.7	0.11	no
Benzene	15	0.0	15.4	1.00	no

Table II.

Comparison of Total System Method Variability (2RSD)
Through-the-Probe Audit Estimate and Collocated Estimate

Compound	Avg. TTP Audit Conc. (ppb)	Avg. Detected [*] Ambient Conc. (ppb)	TTP Estimate (%)	Collocated Estimate (%)
DCM	2.4	1.4	31.7	44.1
CHC13	0.35	0.03	41.2	37.1
CCL4	0.24	0.12	25.0	15.3
EDC	1.1	<0.2	69.5	NA
TCEA	1.1	0.9	64.6	76.7
EDB	0.24	<0.01	31.3	NA
TCE	1.0	0.17	21.7	125.6
Perc	0.32	0.27	29.4	28.1
Benzene	2.4	2.4	30.7	24.5
Butadiene	NA	0.34	NA	23.8

* Average detected ambient concentration is calculated using ambient data above the limit of detection (> LOD) only.

Figure 1. Diagram of the "Through-The-Probe" Audit System

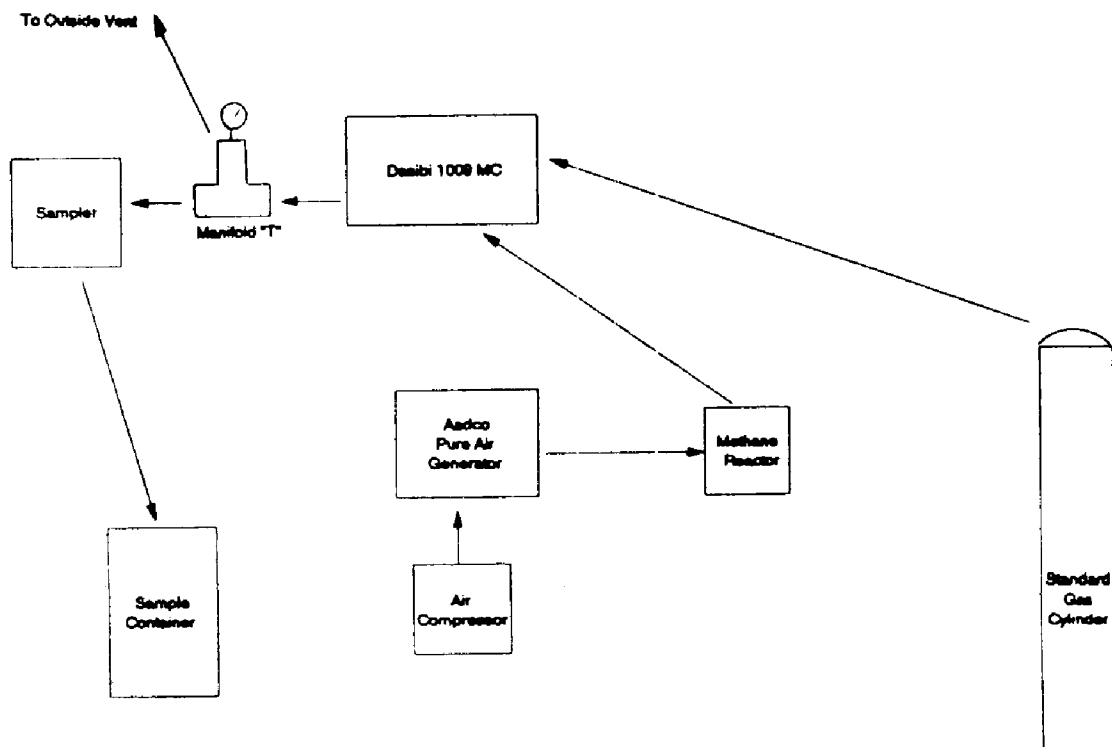


Figure 2.

**Toxic Air Contaminant Accuracy and Precision
(Based on 1989 - 1990 Through-The-Probe Audit Results)**

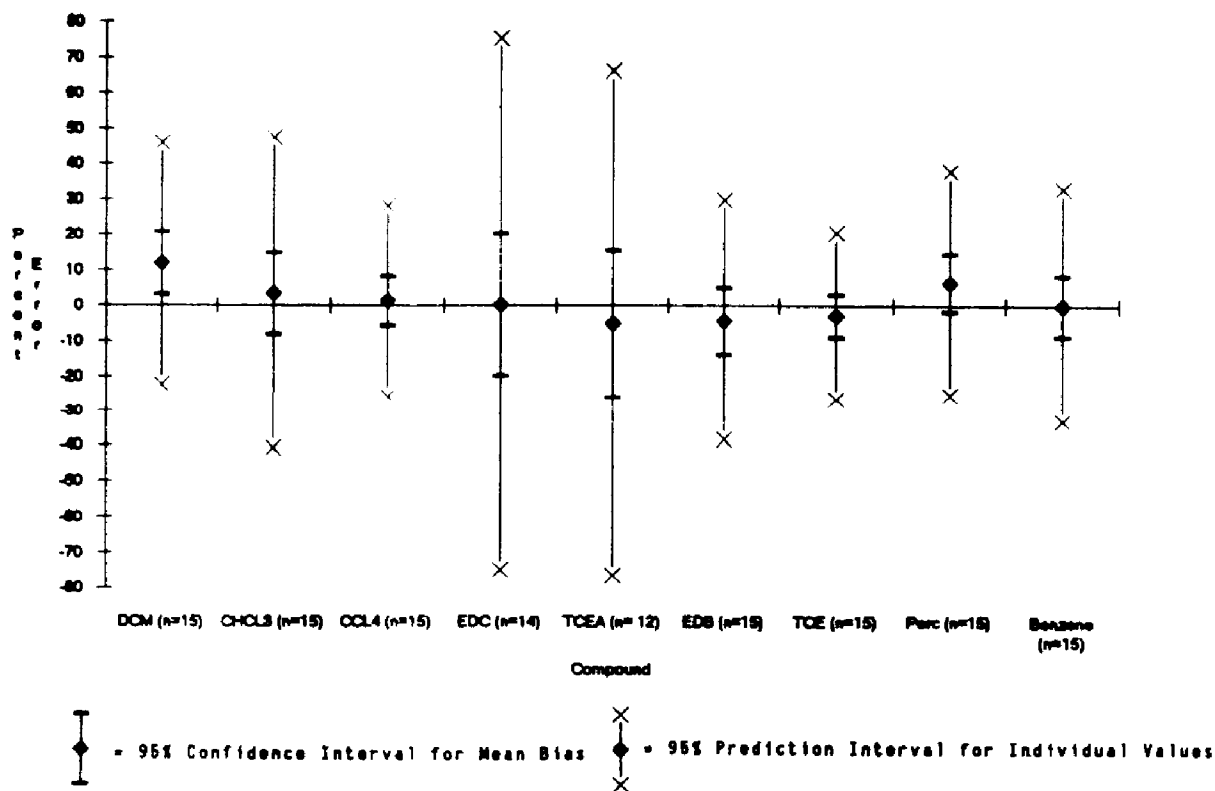


Figure 3.

**Through-The-Probe Audits 1989 - 1990
Dichloromethane (DCM)**

Average Detected Ambient Concentration = 1.4 ppb
Average TTP Audit Concentration = 2.4 ppb

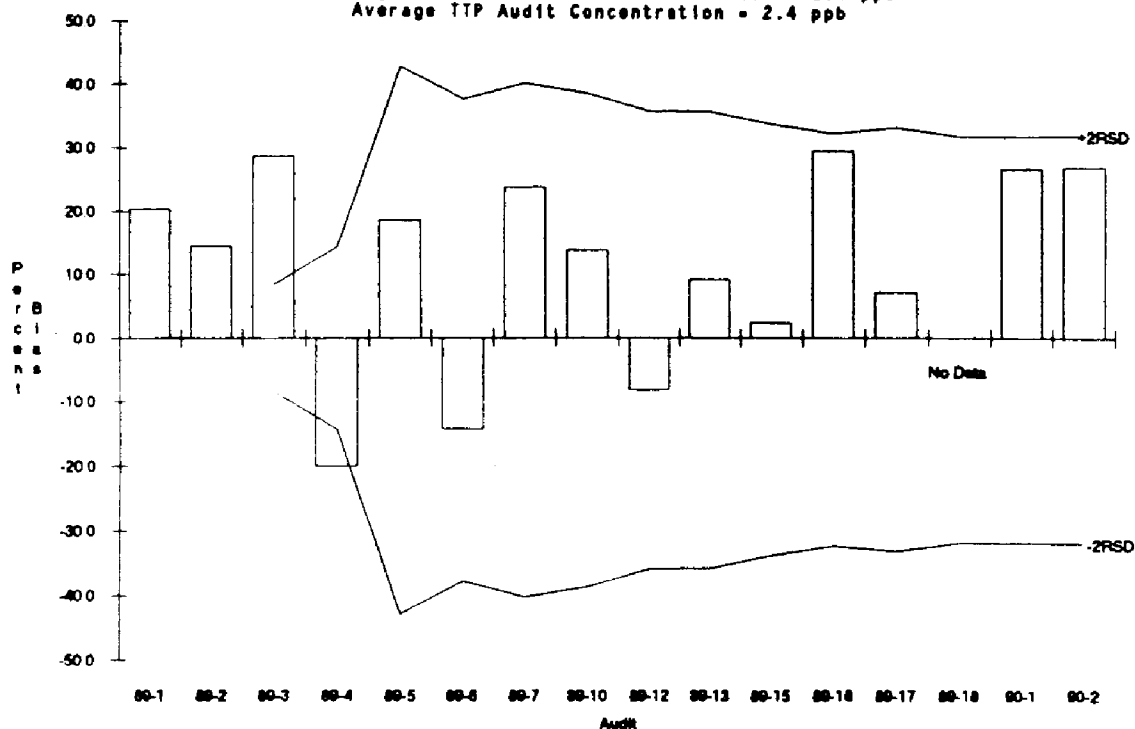


Figure 4.

Through-The-Probe Audits 1989 - 1990
Chloroform (CHCl₃)

Average Detected Ambient Concentration = 0.03 ppb
Average TTP Audit Concentration = 0.35 ppb

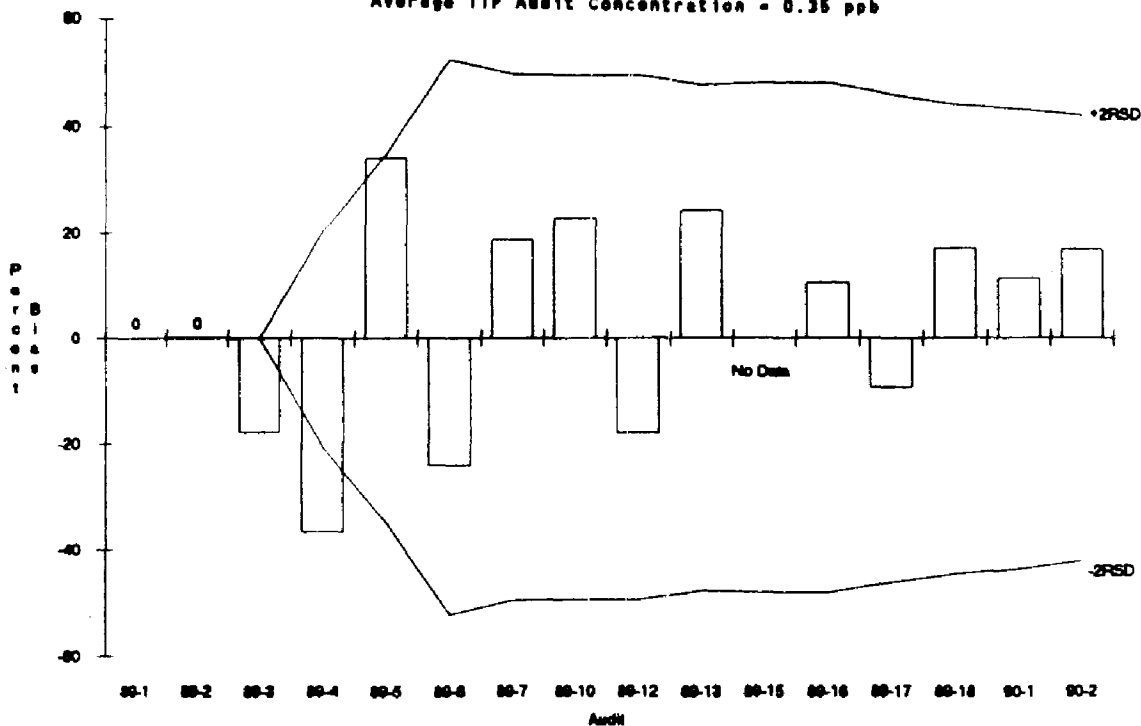


Figure 5.

Through-The-Probe Audits 1989 - 1990
Carbon Tetrachloride (CCl₄)

Average Detected Ambient Concentration = 0.12 ppb
Average TTP Audit Concentration = 0.24 ppb

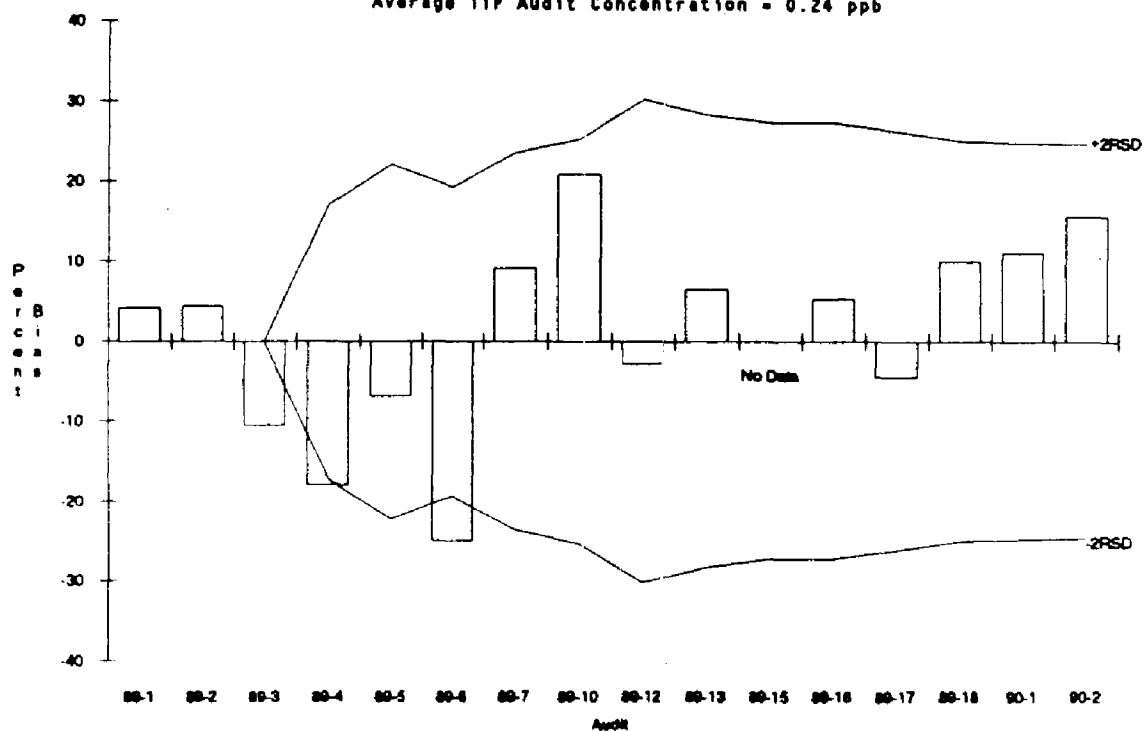


Figure 6.

Through-The-Probe Audits 1989 - 1990
Ethylene Dichloride (EDC)

Average Detected Ambient Concentration = <0.2 ppb
Average TTP Audit Concentration = 1.1 ppb

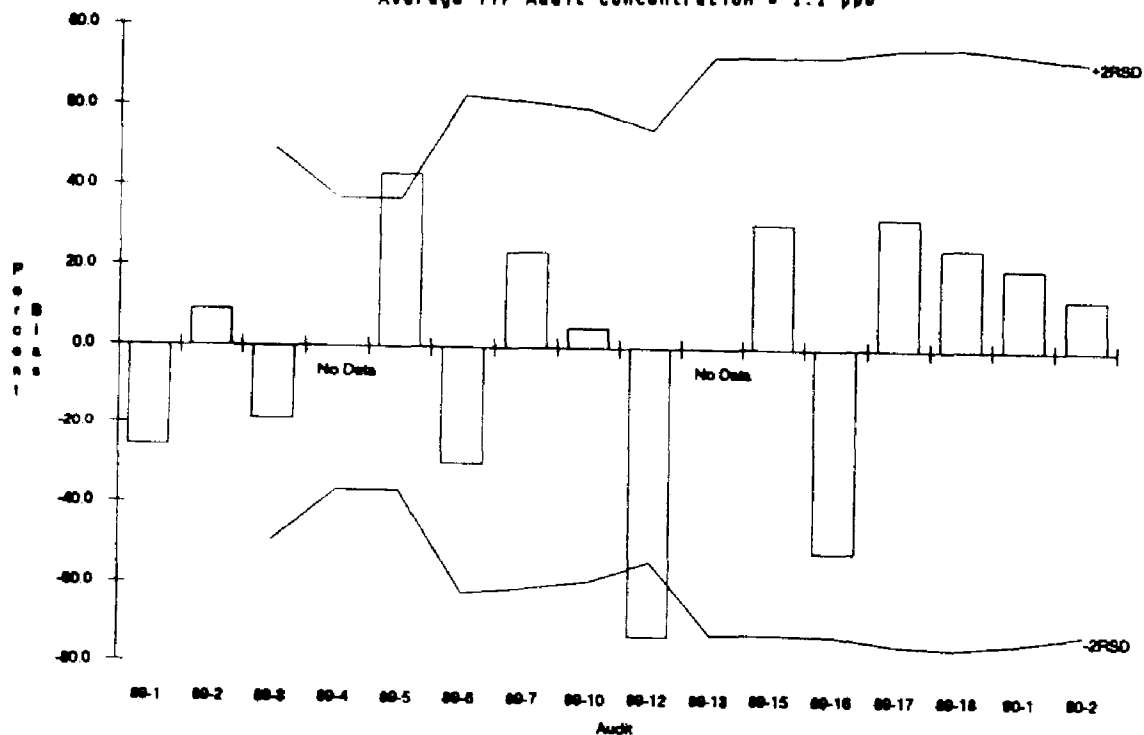
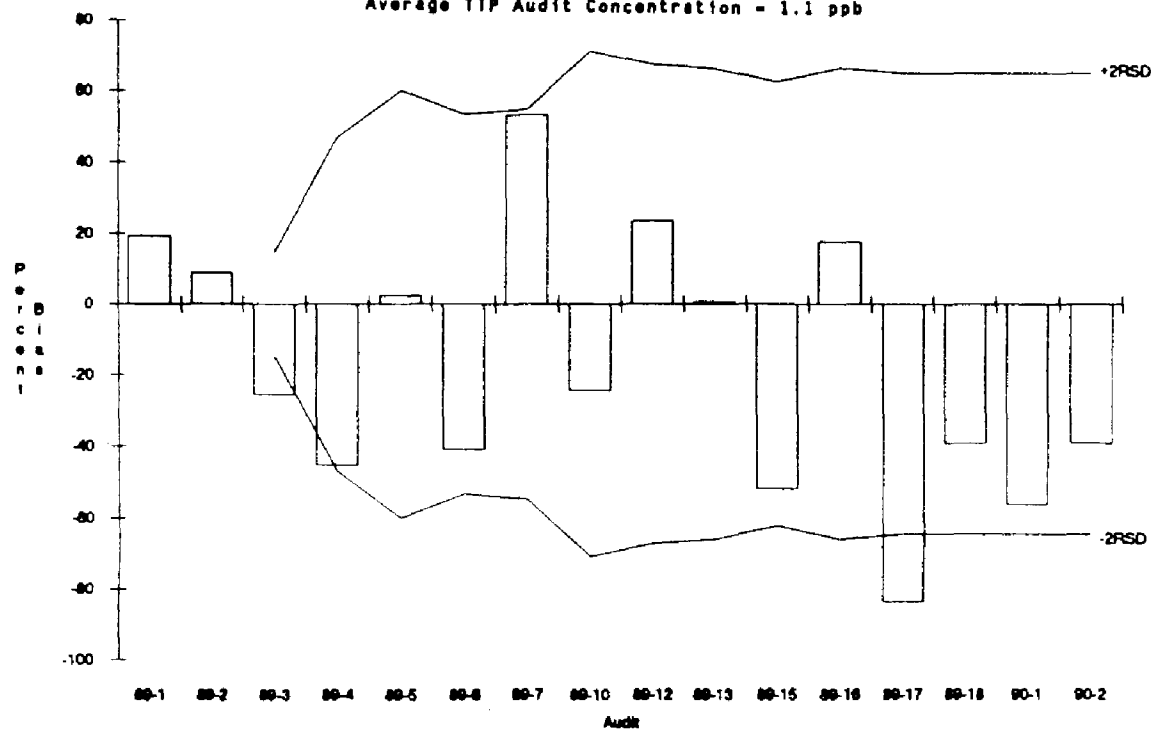


Figure 7.

Through-The-Probe Audits 1989 - 1990^{*}
1,1,1-Trichloroethane (TCEA)

Average Detected Ambient Concentration = 0.9 ppb
Average TTP Audit Concentration = 1.1 ppb

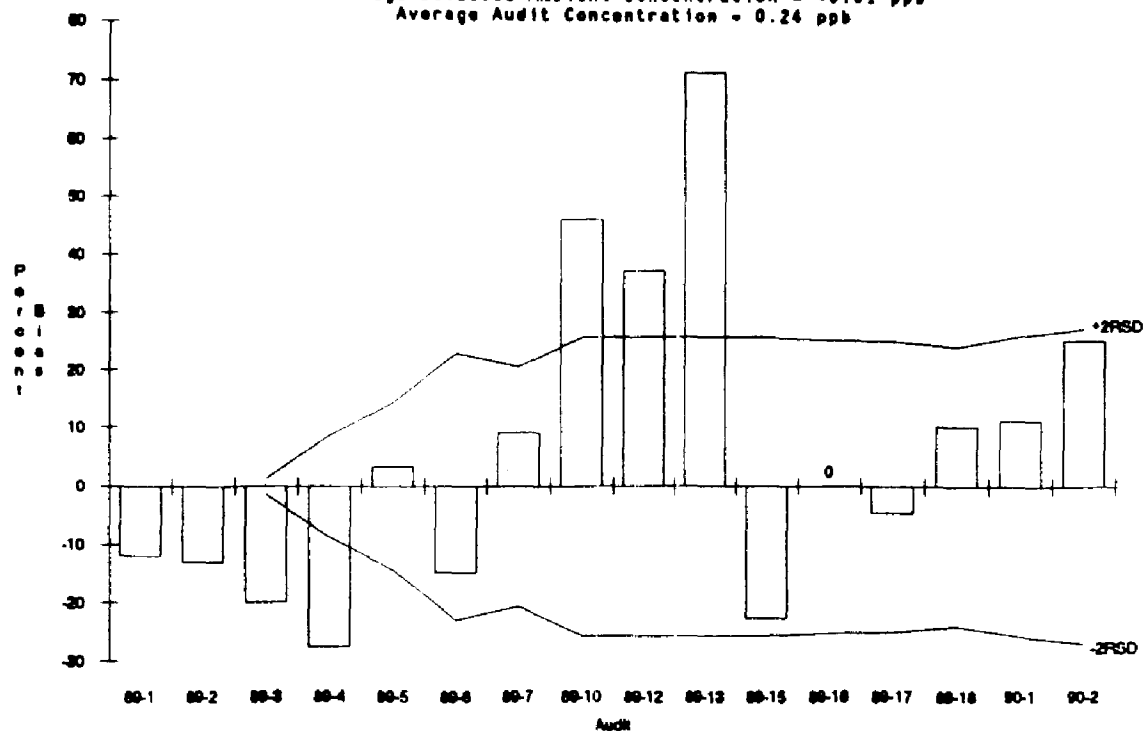


^{*} Audits 89-17 through 90-2 not included in data screening (2RSD) lines.

Figure 8.

Through-The-Probe Audits 1989 - 1990^{*}
Ethylene Dibromide (EDB)

Average Detected Ambient Concentration = <0.01 ppb
Average Audit Concentration = 0.24 ppb



* Audits 89-10 through 89-13 not included in data screening (2RSD) lines.

Figure 9.

Through-The-Probe Audits 1989 - 1990
Trichloroethene (TCE)

Average Detected Ambient Concentration = 0.17 ppb
Average TTP Audit Concentration = 1.0 ppb

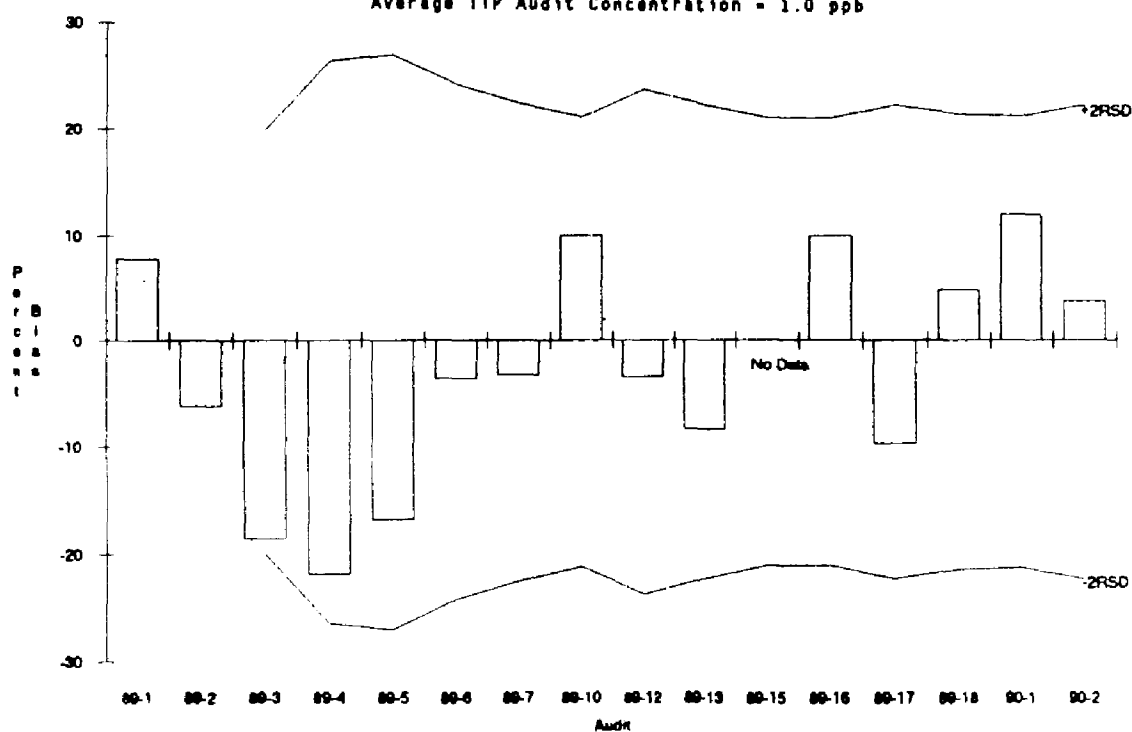


Figure 10.

Through-The-Probe Audits 1989 - 1990
Perchloroethylene (Perc)

Average Detected Ambient Concentration = 0.27 ppb
Average TTP Audit Concentration = 0.32 ppb

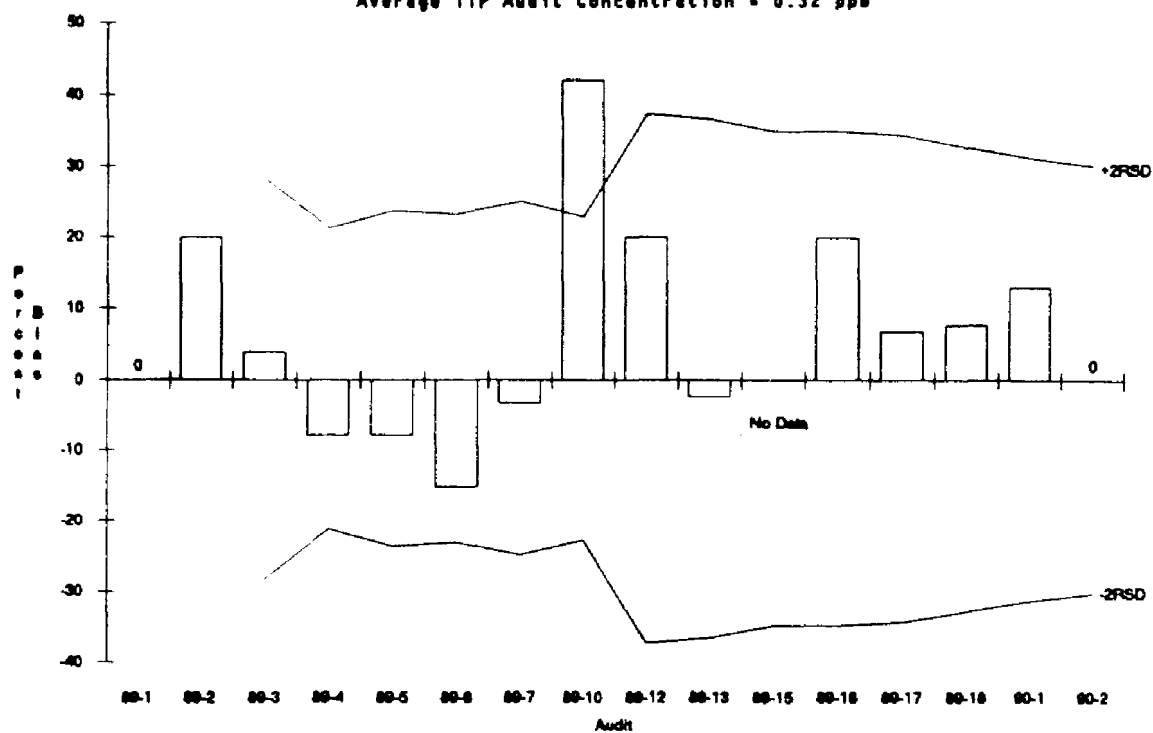
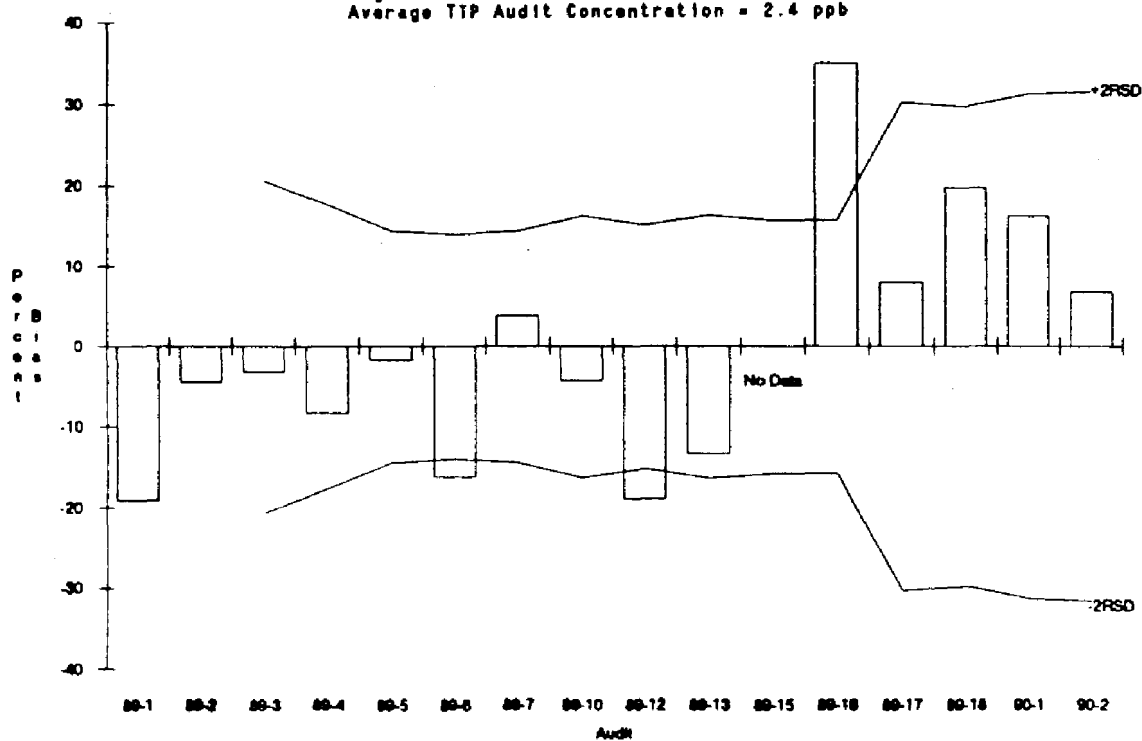


Figure 11.

Through-The-Probe Audits 1989 - 1990
Benzene

Average Detected Ambient Concentration = 2.4 ppb
Average TTP Audit Concentration = 2.4 ppb



**Uncertainty Estimates for the NAPAP
Material Exposure Monitoring Network Data**

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Abstract

This materials effects study was conducted to provide research data for the National Acid Precipitation Assessment Program (NAPAP), to determine the effects of acid precipitation on materials, and to aid in the development of models describing damage to air quality (concentrations of SO_2 , O_3 , NO_2 , NO , NO_x) and certain meteorological variables (temperature, humidity/dewpoint, and wind speed).

To determine the accuracy of the models, it was necessary to estimate the uncertainty of the aerometric variables using quality assurance (QA) data. Performance and system audits were conducted on the Materials Exposure Monitoring sites by Research Triangle Institute, under contract to the Environmental Protection Agency. A total of five QA audits were conducted over a 4-year period, from 1985 through 1988.

Two methods were used in making the uncertainty calculations. In the first method, the data were fit to simple linear regressions so that the uncertainties could be estimated using the confidence limits on the regression at specific concentrations. In the second method, uncertainties were estimated from statistics calculated on the differences between the site and audit concentration measurements. The two methods produced consistent results.

Introduction

A field exposure study investigating the effects of acid deposition on materials damage was performed by Task Group VII (Effects on Materials and Cultural Resources) of the National Acid Precipitation Assessment Program (NAPAP). Samples of various materials were exposed to the environment at five field sites in the eastern United States. Air quality (including particulate concentrations), meteorology, and rain chemistry [provided by Bureau of Mines (BOM)] were measured continuously to allow accurate assessment of the quantitative effects of acid deposition on materials.

The purposes of this study were to (1) determine the extent of damage due to acid deposition on materials, and (2) aid in the development of models describing the materials effects damage. The models relate materials damage to air quality parameters (such as concentrations of SO_2 , O_3 , NO_2 , and NO_x) and meteorological parameters (such as temperature, wind speed, and humidity/dewpoint).

Introduction

The extraction of organic pollutants from environmental solids including sorbent resins, air particulates, sediments, and soils, is often the slowest and most error-prone step of an entire analytical scheme. It is ironic that, while chromatographic methods can separate, identify, and quantitate hundreds of individual species per hour, the most frequently used sample extraction method (liquid solvent extraction in a Soxhlet apparatus) was in common use when Tswett first reported chromatography in 1906. Besides requiring several hours to perform, liquid solvent extractions yield samples that often need to be concentrated, result in large volumes of waste solvent (and exposure of laboratory personnel to potentially harmful solvents), and can introduce considerable error into the final analytical result.

Supercritical fluids have several characteristics that make them useful for analytical-scale extractions of organic pollutants from solid matrices:

- 1) Supercritical fluids have solvent strengths that approach those of liquids but, in contrast to liquid solvents, the solvent strength of a supercritical fluid can easily be controlled by the pressure (and temperature) of the extraction. Extraction at lower pressures (e.g., 80 atm) favors less polar analytes while higher pressure extractions (e.g., 400 atm) favors more polar analytes.

- 2) Mass transfer in supercritical fluids is ca. two orders of magnitude faster than in liquids. Thus, SFE can be completed much faster than conventional liquid solvent extractions.

- 3) Supercritical fluids such as CO_2 , N_2O , and SF_6 are gases at ambient conditions, which simplifies sample concentration steps and makes the direct coupling of SFE with capillary GC simple to perform.

Experimental Methods

Supercritical fluid extractions were performed using syringe-type supercritical fluid pumps (Suprex and ISCO) and either CO_2 , N_2O , or CO_2 with added methanol modifier. Supercritical pressures were maintained inside the extraction cells (0.1 to 10 mL depending on sample size) with 15 to 30 μm i.d. X 150 μm o.d. fused silica capillary tubing for outlet restrictors. Temperature was maintained during extraction by inserting the cell into a thermostatted tube heater. For non-coupled SFE, the extracted species were collected by inserting the outlet restrictor into a vial containing 2 mL methylene chloride. GC/FID and GC/MS analyses of these extracts were performed in a normal manner. The direct coupling of the supercritical fluid extraction step with gas chromatography (SFE-GC) was achieved by inserting the SFE outlet restrictor directly into the capillary gas chromatographic column through the on-column injection port (on-column SFE-GC) or by inserting the restrictor into a split/splitless injection port through an SGE septumless injector (split SFE-GC). Extracted species were cryogenically trapped in the gas chromatographic column which was held at -30 to 5°C. After the extraction was completed, the restrictor capillary was withdrawn from the injector and gas chromatographic analysis was performed in a normal manner.

The Atmospheric Research Effects and Assessment Laboratory (AREAL) of the U.S. Environmental Protection Agency (EPA) supported this effort by the creation and maintenance of the Materials Aerometric Data base (MAD). AREAL has a contract with Computer Sciences Corporation to maintain, analyze, and validate the data constituting the MAD. The MAD contains air quality and meteorological data, measured at the five exposure sites. On-site system and performance audits were conducted by Research Triangle Institute (RTI) at each of the five sites.

Materials Effects Study

Continuous measurements of the air quality, meteorological, and particulate data were made at five field exposure sites, including the following:

- | | |
|---|-------------------------|
| • Sulfur dioxide (SO ₂) | • Wind direction vector |
| • Ozone (O ₃) | • Temperature |
| • Oxides of nitrogen (NO _x) | • Dew point |
| • Nitric oxide (NO) | • Relative humidity |
| • Nitrogen dioxide (NO ₂) | • Precipitation |
| • Wind speed average | • Solar radiation |

The deposition of these species of pollutants in the presence of water or water vapor leads to the corrosion of exposed materials.

The locations of the material effects sites were located in Newcomb, NY; Chester, NJ; Steubenville, OH; Washington, DC; and RTP, NC. A description of the specific sites and monitoring instrumentation has been previously reported [1,2]. The formats and detailed summaries of the data are described elsewhere [3,4]. A summary of the SO₂ concentrations for the sites for 1985-1987 is given in Table I.

Materials Exposure Network Audits

Audits were conducted over a 24-hour period, initially just once a year for each site but, increasing to twice a year during the latter years of the study. On-site audits were conducted over a four year period from 1985 to 1988 for a total of five audits during the study [5].

The purpose of the audit was two-fold: (1) to furnish a means of rapidly evaluating the specific operations atmospheric measurement and data recording devices at the sites, and (2) to provide a continuing index of the validity of site environmental data.

Prior to the audit, all auditing systems were verified at RTI and/or EPA using traceable and/or known standards. The gaseous analyzer auditing system was verified using analyzers calibrated with the National Institute of Standards and Technology (NIST) Standard Reference Materials (SRMs) and/or primary standards. The flow rate auditing devices were verified (calibrated) using primary volumetric standards. The meteorological auditing systems were verified (calibrated) by either the manufacturer or by using primary standards.

On-Site Audit Procedures

Gaseous Analyzers: The on-site audit procedure for the gas analyzers consisted of challenging the monitors with pollutant concentrations over two

ranges:

- (1) 0 to 25 ppb and (2) 0 to 500 ppb.

The lower range is representative of actual ambient air conditions, while the higher range is comparable to other QC/QA activities conducted at the site.

Test levels of O_3 were generated using an ultraviolet ozone generator as described in the Code of Federal Regulations, Appendix D of Part 50. Test levels of SO_2 were generated using dynamic dilution. NO and NO_2 test levels were generated using cylinder dilution and gas phase titration, respectively.

Meteorological Instrumentation: The audit procedure for meteorological sensors was to collocate audit sensors. A data logger was used to record not only the auditing sensor signal, but also the site sensor's signal to ensure compatibility in data reduction procedures.

Particle Collection Devices: A high volume orifice was used to audit the flow rate of the high volume samplers. Two calibrated orifices were used to audit the total, fine, and coarse flow rates of the dichotomous samplers.

System Audit and Data Acquisition: A systems audit was conducted according to guidelines given in the Quality Assurance Handbook for Air Pollution Measurement Systems, Vol. II, [6]. Important points which were considered during the on-site evaluation included (1) evaluation of site according to EPA siting criteria, (2) set up of continuous monitors and meteorological instruments, (3) availability and suitability of the calibration system, and (4) check of the site operator's recordkeeping and documentation including traceability of calibration standards.

Collocation of ambient air data and meteorological data collection were conducted with a Fluke Model 2280a data acquisition system. This system was programmed to scan every 10 seconds and calculate hourly averages. Using these data (volts) and the calibration relationship as provided by the site operator, a comparison was made between hourly data reported by the site and hourly data acquired during the audit. Differences between the hourly averages and standard deviations of the differences were calculated and reported [5].

Audit Results: After each site audit, the findings were discussed between the audit team and the site operators so that corrective action could be taken immediately. Upon completion of the audit, these findings were presented to EPA management to insure that corrective action had been taken at each site. Linear regression coefficients were calculated, assuming linearity of the site analyzers. The criteria for evaluation of the gaseous analyzers were based on the calculated slope and intercept, as follows:

Satisfactory = $0.85 \leq \text{slope} \leq 1.15$, $-3\% \text{ full scale} \leq \text{intercept} \leq +3\% \text{ full scale}$

Unsatisfactory = $\text{slope} < 0.85 \text{ or } > 1.15$, and $< -3\% \text{ full scale or } > +3\% \text{ full scale}$.

The criteria for evaluating the meteorological instrumentation were based upon the recommended tolerance limits as given in the Quality Assurance Handbook Vol. IV [7]. The performance of the particle samplers was based on the average percent difference in flow rates:

Satisfactory = % difference < $\pm 10\%$

Unsatisfactory = % difference > $\pm 10\%$

Uncertainty Estimation

The audits described above provided data which were used to estimate the measurement uncertainties. In the following discussion we will limit ourselves to SO₂ uncertainties.

A preliminary method of data analysis is to plot the site measurement versus the audit concentration levels to look for trends. For an accurately calibrated instrument, the plot would be a straight line with a slope of 1, with the site measurement exactly correlated to the audit concentration.

Differences between the site measurement and the audit value were calculated for each pair of data within the concentration ranges. In this case, the differences themselves represent the uncertainty of the site measurements.

$$D_i = Y_i - X_i$$

Y_i is the site measurement, and

X_i is the audit concentration or measurement

The average of the difference can be attributed to the calibration bias of the site instrument. The standard deviation of the differences represents actual measurement variability of the site instrument. The average difference (\bar{D}) and the standard deviation of the difference (σ_d) were calculated for each concentration range using:

$$\bar{D} = (\sum D_i)/n$$

$$\sigma_d = [((\sum (D_i - \bar{D})^2)/n)]^{1/2}$$

The average and standard deviation correspond to separate error components and must be combined to estimate the uncertainty. Another statistic which can be calculated is the quadrature of the deviation. The method of quadratures is used in the propagation of error to combine errors from different sources. The equation for calculating the uncertainty by quadrature (QDEV) is

$$QDEV = [\bar{D}^2 + (2\sigma_d)^2]^{1/2}$$

The factor of 2 in front of σ_d corresponds to two standard deviations used for the 95% confidence level. The quadrature may not be an independent estimate of error leading to an overestimation of the error. The QDEV also does not take advantage of the fact that the average difference should be zero.

An additional statistic which can be calculated for these data is the squared deviation of the difference from zero (DEVO). An exact measurement of the DEVO would be zero. The equation for calculating the uncertainty by squared deviation from zero is given below:

$$DEVO = 2 [(\sum (D_i)^2)/(n-1)]^{1/2}$$

The factor of 2 corresponds to two standard deviations used for the 95% confidence level. The DEVO places all of the variation into a single number calculated directly from the differences. It also takes advantage of the fact that the "true" mean of the differences should be zero.

Results

Table II contains the uncertainty estimates for the indicated analyzer concentrations using the two methods described above.

The QDEV displays lower values at lower concentrations, giving a better approximation to the spread in the real data. The average DEVO did not provide consistent results between sites, but did provide estimates representing the spread of the real data.

For the air quality variables, in this case SO₂, the QDEV and the DEVO displayed increasing spread in the data for higher values. Both QDEV and DEVO measure the uncertainty in slightly different ways and give similar results. Since both statistics are conservative, the best estimate of the uncertainty is the minimum of the pair.

Conclusion

Uncertainties for SO₂ means are given in Table III. These uncertainties were calculated using the QDEV estimates, averaged over the indicated range of ambient air concentrations. The uncertainties in the lowest range are on the order of 5 ppb, which is comparable with the instrument capabilities. The calculations indicated that uncertainty estimates should be used on a site-by-site basis.

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5. R.C. Shores and R.W. Murdoch, "Performance Audit of the Material Exposure Air Monitoring Network," Five RTI Technical Reports, Research Triangle Institute (1985-1988).
6. Quality Assurance Handbook for Air Pollution Measurement Systems: Volume II, Ambient Air Specific Methods, U.S. Environmental Protection Agency.
7. Quality Assurance Handbook for Air Pollution Measurement Systems: Volume IV, Meteorological Measurements, U.S. Environmental Protection Agency.

Table I. MAD SO₂ concentrations summary for 1985-86-87*

	DC	NC	NJ	NY	OH
Mean	11	3	6	2	22
Min	0	0	0	0	0
Max	143	80	188	29	500

* Values in ppb.

Table II. Uncertainty of SO₂ data, Washington, D.C. exposure site*

Conc.	QDEV	DEVO	Conc.	QDEV	DEVO
0	6	9	0	7	10
5	7	9	50	7	8
10	7	9	100	11	13
15	9	11	200	17	21
20	8	10	300	27	32
			500	42	51

* Values in ppb.

QDEV = Quadrature of deviation.

DEVO = Square root of the average squared deviation from zero.

Table III. MAD SO₂ uncertainties by concentration (in ppb)

Concentration Range	DC	NC	NJ	NY	OH
0 - 5	6	7	4	2	8
5 - 20	7	11	6	6	8
20 - 100	9	12	14	18*	10
100 - 200	14	16*	15	37*	22
200 - 300	22*	20*	16*	46*	41
> 300	34*	24*	22*	68*	61

*Uncertainty estimates above maximum reported ambient air concentration.

QUALITY ASSURANCE FOR CONTRACT SOURCE TESTING
IN THE SOUTH COAST AIR QUALITY MANAGEMENT DISTRICT
(CALIFORNIA)

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The South Coast Air Quality Management District (SCAQMD) conducts about 500 stationary source tests each year. To augment and expand SCAQMD's testing capabilities to 750 source tests, required additional tests are performed through contract laboratories. This paper discusses the various activities in Quality Assurance (QA) for the Source Test Contracts Program in the SCAQMD.

Developments leading to the establishment of the QA program are enumerated and discussed including a review of QA that applies to fundamental principles and methods for the attainment of accurate and reliable results. The discussion includes some of the specific factors and elements of the QA Plan such as pretest preparation, sample collection and analysis, data reporting and validation, calibration, concurrent testing and audits. Also entailed are the QA reporting process and practices, development of audit findings, evaluations, recommendations, implementation of corrective actions, and follow-up resolutions.

As an integral part of the QA program, procedural guidelines and specific criteria for system and performance audits have been established and performed. Also discussed are guidelines and criteria addressing the evaluation of acceptability, validity of data and adequacy of documentation in contract source test reports.

Introduction

In January 1987, the South Coast Air Quality Management District implemented a program after nearly two years of development that would allow contractors to perform a portion of the stack emissions tests conducted by the District to determine source compliance with air pollution rules and regulations. This program utilized pre-qualified, established Engineering firms as contractors selected through an open competitive bid process. Contracts were awarded based upon fixed-price bids for nine separate groups or zones of sources (nominally 25 sources per zone). The zones contained sources grouped geographically that included glass melting furnaces, asphalt batch plants, aluminum furnaces, cement plants, foundries, gas turbines, boilers and various other industrial processes or equipment.

Testing was limited to measurements for particulate matter concentration, carbon monoxide, oxides of nitrogen (NO_x), sulfur dioxide (and other oxidized sulfur compounds), lead concentration, oxygen, water content and mass emission rate. The South Coast District test methods were specified for all tests except those in which New Source Performance Standards (NSPS) were applicable. The NSPS tests were performed according to the appropriate Federal (EPA) test methods as found in the Code of Federal Regulations, Title 40, Part 60.

The Quality Assurance Program was designed to ensure that all testing performed under the contracts program met the high standards required for compliance determinations. This program consisted of: A quality assurance plan relating quality controls such as standardized testing methods or report formats to acceptability requirements; performance audits to challenge the accuracy and precision of contractor test data; field audits to enhance contractor performance; final report evaluations to validate and approve contractor results; and source facilities follow-up to resolve any safety or testability concerns encountered at the designated contract sources.

Discussion

The Quality Assurance Plan was prepared to provide the contractors and District staff with an organized description of the quality information and activities required by the Source Test Contracts Program. The plan included a brief project description, program staff organization (District), distribution list and an outline of the Quality Assurance program. Included in the Quality Assurance program were: Pretest preparation; sample collection and analysis; data reporting and validation (with detailed chain-of-custody procedures); calibration procedures; audits and concurrent testing; and, other considerations (scope of quality assurance activities and an amendment to the test method for lead (Pb) analysis to clarify contractor requirements). The plan also included guidance for the determination of compliance with District Rule 217 - Provision for Sampling and Testing Facilities. This information was provided to promote universal understanding and consistency in evaluations of the testing facilities for sources to be tested by the contractors.

The Quality Assurance Program was conducted in an intensely proactive manner in order to maximize the benefits of Quality Assurance information to contractor personnel and to minimize the number of rejected source tests. Contractors were not paid for any source tests performed until the final source test report was evaluated and approved by the District Quality Assurance Manager. This rather strict control was necessary to ensure that compliance information generated through the Source Test Contracts Program was reliable and equivalent in quality to that produced by the District in-house source test group. Proactive field auditing allowed contractor personnel to receive real-time input from quality assurance staff regarding test methods, District policies, engineering practices or format requirements. Application of this input by the contractors to the in-progress tests significantly reduced the number of rejected final reports.

Field Audits by District quality assurance staff provided validation for the subsequent contractor source test reports; verification of contractor skills and capabilities; and technical support to the contractors. The field audits utilized extensive checklists specific to the various test methods being used for the source test. Pertinent observations, comments and interactions were included on the audit form as well as recommendations for enhanced performance. The field auditors performed another very important function, particularly during the implementation year of the program. Source operators or plant managers reluctant to accept contractor testing for District Rules compliance determinations could interact directly with District auditors who would, in turn, act as "buffers" to facilitate the completion of the source tests.

Pretest preparation included site-specific evaluations to assess the safety and technical adequacy of the sampling facilities (can the test be performed in a safe and technically reliable manner?) and contractor planning to ensure that appropriate personnel and equipment were allocated for the test. Source samples collected for the determination of particulate matter require isokinetic (collection of particulate matter at the same velocity as that of the stack gases) sampling. This implies that the stack gas velocity profile is steady without excessive turbulence or cyclonic flow. The selection of appropriate sampling locations is a necessary prerequisite to the reliable measurement of particulate matter from emission sources. Safety practices followed by the District may have been more extensive than those followed by contract firms in the course of their normal field testing. Guardrails, caged ladders, adequate platforms and appropriate sampling ports were installed in order to provide safe access and sampling conditions. District test methods require specific procedures to be followed so that follow-up actions will be enforceable and legally valid. Due to the rigidity of District testing protocols, contractors had to place considerable emphasis upon pretest evaluation and planning. The contractors used the information gained to compensate for the loss of flexibility (in the field) to modify methods, equipment or techniques to adjust for unforeseen conditions.

Performance audits were conducted to assess the analytical performance of the contractors. These audits consisted of "blind" (preanalyzed samples submitted without indicating concentration values) audit materials and user-friendly audit forms were developed specifically for this program. The audit samples simulated:

- 1) SO₂ and SO₃ collected in an impinger train
- 2) NO₂ collected in a glass bulb/absorbing solution
- 3) Preweighed particulate filters
- 4) NO_x, SO₂, CO, CO₂ and O₂ in compressed gas cylinders to simulate extractive stack analysis by continuous monitoring instruments (Mobile Source Test Vehicles or MSTV's)

Comparative data was also collected by field auditors to evaluate temperature, stack gas velocity and physical dimension measurements through the use of a traceable temperature reference, standard pitot tube and measuring tape. A limited number of parallel source tests between District and contractor test teams provided additional verification of the overall contractor reliability.

Report evaluation and approval were the most significant and effective broad-based quality controls in the program. By linking the payments to contractors for work performed with District approval of final test reports, the quality of contractor testing could be very effectively managed. Final source test reports submitted by contractors were thoroughly reviewed by District Quality Assurance Branch staff to confirm that the appropriate test methods, equipment, plant process conditions, and technical accuracy requirements were followed. Reports found to be substandard were either returned to the contractor for revisions or they were rejected. In some cases, however, reports from tests conducted under less than optimal conditions were approved for information purposes only. These reports were evaluated on a case-by-case basis with the decision being based upon District need for the information, the scope of the test deficiencies and the extent of the efforts made by the contractor to meet all specified test requirements. The test report approval consisted of an approval as to form by the contracts coordinator and the final approval/release for payment by the Quality Assurance Manager.

Formalized contractor source test report audits as well as annual quality assurance reports on the Source Test Contracts Program provided the opportunity to evaluate the contractors over a broad range of activities in a very detailed manner. In the report audits, twenty contractor source test reports were selected at random and thoroughly reevaluated according to previously established criteria. Significant findings were reviewed to determine technical validity as well as impacts on test quality or reliability. Annual quality assurance reports summarized the progress of the program for District management and administrators. This information was used to support the reallocation and funding of the program as part of the budgetary process.

Summary

The quality assurance program developed by the South Coast Air Quality Management District for source emissions testing by contractors was designed to validate the source test data and reports generated by the program.

Concern over the technical adequacy and legal enforceability of contractor produced compliance information resulted in extensive, comprehensive quality assurance requirements for the contractors, their resulting source test activities and final test reports.

The program consisted of a quality assurance plan summarizing quality requirements for contractor performance, various types of audits covering all of the technical aspects of the program and evaluations of contractor performance and reports as well as source facilities. Follow-up actions were taken, as needed, to ensure that testing and reports maintained a high level of quality and reliability and that any observed weak areas were resolved and not recurrent.

The Source Test Contracts Program has been proven to be an effective adjunct to the South Coast District's source emissions compliance testing program due, in part, to a comprehensive, proactive quality assurance program.

Acknowledgement

Many thanks to Dipak Bishnu and John Higuchi for their work in the development and administration of the SCAQMD Source Test Contracts Program.

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- 3) "Audit Procedures for Source Emissions Testing", Quality Assurance Branch, South Coast Air Quality Management District, August 1987.
- 4) Source Test Manual, Technical Services Division, South Coast Air Quality Management District, March 1989.

Results

Supercritical fluid extraction (SFE) reduces the time needed for the extraction of organic pollutants from sorbent resins and air particulates to 5-30 minutes compared to several hours required for conventional liquid solvent extractions. When supercritical fluids are used that are gases at ambient conditions (e.g., CO₂ and N₂O), SFE essentially eliminates the generation of waste solvents, as well as the need for sample concentration steps. The direct coupling of SFE with capillary GC (SFE-GC) allows an entire analysis including sample collection, extraction, analyte concentration, and gas chromatographic separation to be completed in a total time of less than 1 hour, as demonstrated by the analysis of roofing tar organics that were collected on polyurethane foam (PUF) sorbent resin near the face of the tar vat operator (Figure 1). On-column SFE-GC also yields maximum sensitivity since 100% of the collected analytes can be transferred to the GC column for analysis.

Spike recoveries, multiple extractions, and the analysis of certified standard reference materials have demonstrated the ability of SFE and SFE-GC to quantitatively extract a variety of organic pollutants including fuel hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), heteroatom-containing aromatics, and polychlorinated biphenyls (PCBs) from Tenax and PUF sorbent resins; and air particulates released from vehicle exhaust, cigarette smoke and wood smoke¹⁻⁶. Figure 2 shows the results of two sequential SFE-GC/MS analyses of cigarette smoke volatiles collected on PUF. As shown by the lack of significant peaks in the second 10-minute SFE extraction, the first 10-minute SFE extraction yielded essentially quantitative recovery of the cigarette smoke organics.

The most convincing demonstration of the ability of SFE and SFE-GC to yield quantitative results is shown in Table I by a comparison of SFE and SFE results for PAHs with the concentrations certified by the National Institute of Standards and Technology (NIST). Note that while the conventional liquid solvent extractions used by NIST required 16 to 48 hours to perform, SFE and SFE-GC extractions required only 10 to 30 minutes per sample, yet quantitative agreement was excellent. With coupled SFE-GC analysis, sample size can also be dramatically reduced since all of the extracted analytes can be transferred to the chromatographic system. For example, SFE-GC/MS analysis of the urban dust sample required only 2 mg, compared to 1 gram required for the NIST method using liquid solvent extraction.

Conclusions

While considerable research is needed to understand and optimize SFE and SFE-GC methods for the rapid and quantitative extraction and analysis of organic pollutants from sorbent resins and environmental solids, the results reported to date¹⁻⁶ clearly demonstrate the potential of SFE and coupled SFE-GC to reduce extraction times to <30 minutes and to eliminate the production of waste solvents. The ability of coupled SFE-GC to quantitatively transfer all of the extracted analytes into the GC column is especially attractive when the analysis of trace organics from small samples is desired.

Table 1
RATING CRITERIA for
SOURCE TEST REPORT AUDIT

Good (G)	:	Valid source test results; adequate documentation to support conformance with District methods & procedures; all data and information are reported as required for source test reports.
Acceptable (A)	:	Validity of test results is acceptable; however, essential documentation and/or data are missing in the report, which are necessary to supplement conformance with District methods & procedures.
Unsatisfactory (U)	:	Test results are considered invalid; test was not conducted according to District methods & procedures.

Table 2
CONTRACT SOURCE TEST and AUDITS PERFORMED

	FY1987-88	FY1988-89
o SOURCE TESTS	193	185
o FIELD AUDITS	5	15
o PERFORMANCE AUDITS	18	9
o SOURCE TEST REPORT AUDITS	19	39
o PARALLEL TESTING	1	2

LAB CERTIFICATION VERSUS IN-HOME EMISSIONS PERFORMANCE OF ADVANCED TECHNOLOGY WOODSTOVES

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Particulate emissions trends were evaluated for three models of catalytic and two models of non-catalytic woodstoves under "in-home" burning conditions during the 1988-89 heating season in the Glens Falls, N.Y. area. The results (averaging 9.4 g/h and 9.4 g/kg) showed about a 55% reduction in emissions compared to conventional woodstoves and demonstrate that the emissions performance of new woodstove technologies has improved compared to that of stoves in earlier field studies. Emissions for the non-catalytic stoves were about 50-55% and for the best performing catalytic stove about 80% lower than conventional woodstoves. Two of the catalytic stove models displayed elevated emissions; in one case a significant degradation trend developed, in the other emissions were elevated throughout the test period. Leaky bypass systems appear to be a major cause as well as catalyst deterioration resulting from lack of flame shielding and inadequate air/fuel mixing.

Field emissions significantly exceed certification values as they have in past studies. Differences in wood loading patterns and stack draft have been identified as possible causes as well as emissions deterioration over time.

INTRODUCTION

During the 1970s, as a response to the Energy Crisis, there was a dramatic increase in the sale and use of residential woodstoves. By the 1980s residential wood combustion had become a major source of particulate pollution, especially in the many woodburning areas where wintertime temperature inversions were common. A marked improvement in combustion efficiency was needed to reduce these air quality problems.

With the introduction of the catalytic combustor for use in woodstoves by Corning in 1980, the production of clean-burning woodstoves appeared feasible. Research and regulatory activity aimed at producing low emissions appliances increased rapidly for both catalytic and non-catalytic designs.

However, because woodstove development and evaluation activities were generally conducted under laboratory conditions, and operating conditions in homes are significantly different from those in the lab, the effectiveness of lab-certified clean-burning technologies under real world "in-home" conditions was unknown. Recent research efforts have been directed toward evaluating "in-home" performance.

A field study, conducted from 1979-1982 in New York and Ohio¹, using both conventional and catalytic stoves, demonstrated that clean-burning catalytic technology can operate effectively under "in-home" conditions and its effects on emissions and efficiency can be dramatically positive. Due to the small sample size, the question of adaptability of this technology to widespread use was not answered. Additionally, monitoring of the catalytic stoves lasted only one season; therefore long-term woodstove component durability was not addressed.

The results of two more recent studies, the first Northeast Cooperative Woodstove Study² conducted in New York and Vermont from 1985-1987, and the Whitehorse Study³, conducted in northwestern Canada in 1986-1987 suggested that while newer technologies did reduce particulate emissions, reduction was less than 50% and emissions values were higher than certification values. Stove durability problems were recognized, but attempts were not made to identify cause-and-effect relationships between failure of specific components and emissions degradation.

The 1988-89 Northeast Cooperative Woodstove Study (NCWS)⁴, summarized herein, was designed to evaluate the latest technologies in comparison with their certification values and evaluate the woodstove durability issue in depth.

OBJECTIVES

The 1988-89 NCWS study attempted to 1) evaluate the effectiveness of certification values as a predictor of the "in-home" emissions levels, 2) attempt to explain certification - field differences, if they exist, 3) identify new woodstove technologies that can significantly reduce particulate emissions (by approximately 80%) under "in-home" conditions, 4) document emissions degradation, should it occur and 3) determine the cause-and-effect relationships of poor emissions performance.

The "in-home" performance of advanced-technology woodstoves was evaluated for woodstoves that met the following conditions:

- 1) The stoves were Oregon DEQ 1988 certified.
- 2) The stoves passed a laboratory stress test which screened for durability.
- 3) The stove installations had adequate draft, and the stoves were sized correctly for the home.

- 4) The homeowners were experienced woodburners. They were given only a minimum of specialized training about their new stoves.

METHODOLOGY

"In-home" sampling of 25 advanced-technology stoves, installed in homes in Glens Falls, N.Y. (7500 degree day winter climate), was conducted for five week-long periods from January through March, 1989. All stoves were new and had been installed in December, 1988. AWES (Automated Woodstove Emissions Sampling) and OMNI Data LOG'r systems⁵ were used to measure particulate stack emissions, thermal efficiency, stack and catalyst temperatures, stack oxygen, stack draft, burn rate and wood use patterns.

Five stove models, three catalytic and two non-catalytic, were selected for the study from a candidate group of ten stoves based on their performance in a laboratory stress test designed especially for this project. Five stoves of each of the five stove models were evaluated in the field.

RESULTS

The overall average burn rate of the new technology stoves was 1.09 dry kg/h. Average wood moisture was 27% dry basis (21% wet basis). And average draft was -0.074 in. water column and average stack oxygen was 15.4%.

The overall average particulate emissions was 9.4 g/h (9.4 g/kg). The lowest emissions woodstove model, the Country Flame BBF-6, a catalytic stove, had average emissions of 4.6 g/h (4.1 g/kg). The emissions of the other four stove models appear statistically to constitute a single population, with emissions about twice as high as the Country Flame's.

A relatively high average net thermal efficiency of 67% was attained by the Country Flame BBF-6 stoves. Efficiencies of non-catalytic stoves were about 50-55% similar to conventional stoves. These lower efficiencies were due primarily to the lower combustion efficiency, relatively high levels of excess air and high stack temperatures characteristic of non-catalytic stoves.

Two of the three catalytic stove models did not perform as well as had been expected. One, the Blaze King Royal Heir, experienced a significant trend in performance degradation which began after one month of stove operation. The other, the Oregon Woodstove, displayed generally elevated emissions performance throughout the test period.

Examination of the stoves during and after the emissions testing period identified the failure of a small number of identifiable components as the cause of emissions degradation, and identified areas of potential premature component failure.

- 1) Blaze King Royal Heir 2200 (catalytic): Warping of some bypass support areas developed, causing leaks around the catalyst. Probable partial catalyst failure occurred in some stoves, induced, at least in part, by lack of flame impingement shielding and high internal catalyst temperatures.
- 2) Oregon Woodstove (catalytic): Bypasses generally fitted loosely, causing leaks around the catalyst. Bypass control mechanisms also would not close the bypass consistently.
- 3) Regency R3/R9 (non-catalytic): Some baffles oxidized and/or warped.
- 4) Country Comfort CC150 (non-catalytic): Oxidation and warping of bypass support areas developed.

CONCLUSIONS

The performance of new technology woodstoves has improved markedly compared to the results reported for stoves in the earlier Northeast Cooperative Woodstove and Whitehorse studies, which were conducted in northeastern U.S. and western Canada. The overall average particulate emissions of 9.4 g/h (9.4 g/kg) for the woodstoves evaluated in the current study represents a 55-60% reduction in emissions compared to the EPA emissions factor of 21.3 g/h⁶ for conventional stoves, and demonstrates that current technology is capable of significantly reducing particulate emissions from woodstoves.

The lowest emissions woodstove model, the Country Flame BBF-6, a catalytic stove, with average emissions of 4.6 g/h (4.1 g/kg), approaches the 1990 EPA certification limit of 4.0 g/h. These emissions are about 80% lower than those of conventional woodstoves.

The emissions of the two brands of non-catalytic stoves, the Regency R3/R9 and the Country Comfort CC150, which average 9.3 g/h (8.2 g/kg) and 11.3 g/h (11.2 g/kg) respectively, are about 50-55% lower than those for conventional stoves, and are higher than the 7.5 g/h 1990 EPA certification limit for these stoves.

"In-home" performance of four of the five stove brands did not agree closely with the certification emissions values, exceeding these values by up to four times as much. On the other hand, the EPA-weighted certification emissions values and the results for the "in-home" tests on the remaining stove brand, the Country Flame BBF-6, were nearly identical.

The field performance of one of the catalytic stove models degraded with time magnifying the discrepancy with certification values. Signs of physical degradation in three of the other models suggest that emissions deterioration may develop with them in subsequent years.

It is concluded that certification emissions values probably continue to understate field performance. There are two identified reasons: 1) certification test conditions are different from those in the field (especially wood loading geometry and stack draft) and 2) the emissions performance of an as yet undetermined number of stove models degrade over time.

Because certain conditions in the field differ from those in the lab, the common practice of using certification testing as a stove design development tool appears to be having a negative impact on stove design. For example, "in-home" burning conditions produce stack gases that are about twice as dilute as those produced by the Douglas fir cribs used in certification tests, and "in-home" drafts are almost twice as high. To perform satisfactorily under certification testing conditions, manufacturers therefore tend to design stoves with more secondary air than is needed in most home burning situations. This excess air creates higher than necessary catalyst temperatures and may shorten the life of catalysts. This situation also encourages the use of smaller diameter catalyst cell sizes. In homes these cells are more prone to clogging and can develop locally higher catalyst temperatures than larger cells do.

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ANALYSIS OF AIR POLLUTANT CONCENTRATIONS BELOW THE DETECTION LIMIT

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Air quality data often contain several observations reported only as below the analytical limit of detection (LOD), resulting in censored data sets. Such censored and/or truncated data sets tend to complicate statistical analysis. We discuss several procedures for estimating the mean concentration and its 95% confidence interval for air contaminant data that contain values below the LOD. A quantitative approach for assessing the uncertainty inherent in the estimated mean concentration due to the presence of values below the LOD in the data set, as well as the natural variability of atmospheric concentration data, is described. The utility of this approach in the analysis and interpretation of air pollutant concentration data is demonstrated for a singly-censored hypothetical data set drawn from a normally distributed population, and for a multiply-censored, multi-pollutant observed concentration data set.

The methodologies discussed here should be particularly useful in estimating the risks associated with long-term exposure of populations to toxic air contaminants, and in assessing the uncertainty associated with these estimates. This information is valuable to policymakers for making informed decisions regarding the environmental risk.

Introduction

Recent advances in ambient air quality monitoring technology are enabling us to measure very low levels of toxic air contaminant concentrations. However, because of inherent limitations of the chemical/analytical methodologies, air quality data sets often contain several observations reported as below the analytical limit of detection (LOD). The presence of values below the LOD results in censored data sets, and complicates all related statistical analyses.

Many of the methods in the statistical literature¹ for analyzing censored data are sensitive to assumptions about the underlying distribution. For a left-censored concentration data set, if LOD values are used in place of actual “net” (as if measured) concentrations, the mean \bar{x} will be biased high (*i.e.*, on the average \bar{x} will be larger than μ , the true mean) and the variance s^2 will be biased low (*i.e.*, s will be smaller than σ , the true standard deviation). Biases will also arise if the values below the LOD are ignored, or if they are replaced by “zeros” before computing the mean and the variance. Another method suggests replacing concentrations below the LOD by the mid-point between zero and the LOD value. In principle, we must regard each of these approaches as unacceptable for one or more reasons if our objective is to obtain unbiased estimates of μ and σ .

The long-term (*e.g.*, the annual mean) concentration of a toxic contaminant must be determined to quantify the risk associated with chronic human exposure. Often, samples of certain pollutants collected over a period of time may be censored at different levels as changes in analytical technology alter the LOD of the selected method. Among examples of this are the ambient measurements for the total 2,3,7,8-TCDD (tetrachlorodibenzo-p-dioxin, commonly referred to as “dioxin”) concentration. Analysis of such multiply-censored, multi-pollutant data is more complex than that of singly-censored data for a single pollutant.

In this paper, we examine selected techniques for the analysis of air quality data which contain values below the LOD. Several methodologies for quantifying the uncertainty associated with the presence of values below the LOD in the data set, and the natural variability of atmospheric concentration data, are examined. The utility of these methods is examined by applying them to a hypothetical data set drawn from a normal distribution, and to an observed data set of multiply-censored, multi-pollutant (dioxin) concentrations.

Quantification of Uncertainty

Uncertainties associated with ambient air quality data (assuming the measurements to be error-free) stem from the fact that (a) the “net” concentrations are always unknown when the data are reported as below the LOD, and (b) any given ambient measurement reflects a single event of a population. Therefore, a 95% confidence interval which describes the limitations of the methodology chosen for treating the data below the LOD, as well as the natural variability in air pollutant concentrations, needs to be estimated for communicating the inherent uncertainty in the estimated mean concentration to a decision-maker.

We utilized the following approaches to “fill-in” for the data below the LOD in estimating the statistical parameter of interest, and the uncertainty associated with this estimate:

- (i) The reported value below the LOD is replaced by a value chosen randomly from a uniform distribution which assumes that any value in the range from 0 to the reported LOD value is equally likely to occur. The region between 0 and the LOD is divided into 10 equal segments, and each segment's mid-point is taken as the concentration value representing that segment. A segment number is randomly selected and the concentration associated with that segment is taken as the net concentration replacing the below-LOD value. This procedure is repeated for all concentrations reported as below the LOD, and the mean concentration and the standard deviation for the total sample are computed.

The above procedure is repeated several (say 100) times, for assessing the variability in the estimated mean concentration of the pollutant. Using the results of 100 Monte Carlo simulations, cumulative distributions for the computed means and the standard deviations are developed, and their medians are then determined. These median values may be considered to represent robust estimates of the statistical parameters of interest for each pollutant.

Once the data set for the year for each pollutant (isomer) is assembled in this manner, the annual mean concentration of a multi-pollutant (*e.g.*, dioxin), \bar{x} , is then computed using the weighted sum of averages as:

$$\bar{x} = \sum_k (w_i \bar{x}_i) \quad (1)$$

where \bar{x} is the weighted sum of k different isomers, the w_i are the weights, and the \bar{x}_i are the means of samples of size n_i for each isomer. The problem of the distribution of a weighted sum was discussed by Satterthwaite², and Gaylor and Hopper³. Assuming independent samples, the 95% confidence interval (*CI*) for the mean can be determined from⁴:

$$CI = \bar{x} \pm t_{(\alpha/2, f)} \hat{\sigma}(c) \quad (2)$$

$$\hat{\sigma}^2(c) = \sum_k (w_i^2 \hat{\sigma}_i^2 / n_i) \quad (3)$$

where $\hat{\sigma}_i$ are the estimated standard deviations of samples for each isomer, t is Student's test statistic, $\alpha = 0.05$ is the level of significance, and f is Satterthwaite's improved degrees of freedom given by:

$$f = \left[\sum_k (w_i^2 \hat{\sigma}_i^2 / n_i) \right]^2 / \sum_k \left[(w_i^2 \hat{\sigma}_i^2 / n_i)^2 / n_i \right] \quad (4)$$

- (ii) The above Monte Carlo simulation procedure is again employed except that the reported below-LOD value is now replaced by a value chosen randomly from a normal distribution (with mean = 0.5 LOD), assuming that the region between 0 and the reported LOD value is bound by ± 3.5 times the standard deviation of the data in this region.
- (iii) The bootstrap method (see Efron⁵; Rao *et al.*⁶) is also employed to fill-in for the values below the LOD and to estimate the 95% confidence bounds for the mean concentration. The procedure entails randomly selecting the concentration values in the region between zero and the reported LOD (assuming

a uniform distribution), and combining them with the detected concentrations to reconstruct the original sample. This reconstructed sample is then subjected to 100 bootstrap replications (random sampling with replacement), and the median of the 100 means and the median of the 100 standard deviations are determined, along with the 95% confidence bounds for the mean concentration based on the percentile method.

Results and Discussion

The limitations associated with the treatment of the values below LOD are assessed by invoking either the uniform or normal distribution approach to fill-in the region below the LOD, followed by Monte Carlo simulation. These procedures are applied to a hypothetical data set with a sample size of 60 values which is drawn randomly from a normal population $N(\mu, \sigma) \equiv N(20, 5)$. The "true" 95% confidence interval for the mean of 60 samples is [18.735, 21.265]. The estimated mean, standard deviation, and the 95% confidence interval for the mean of the original sample from the normal distribution are given in Table I. The 95% confidence bounds for the mean of the original sample are also determined using the nonparametric bootstrap resampling method (see Rao *et al.*⁶). As to be expected, the estimated mean deviates from the mean of the original sample, as the level of censoring increases. The results indicate good agreement among the sample means and their upper 95% confidence limits determined from different methods for this data set.

The above approaches to fill-in for the values below the LOD were applied to the atmospheric dioxin concentration data collected during the period from September 1986 to March 1988 in Niagara Falls, New York. A listing of the 24 different isomers which were measured, and their weightings (based on toxicity) in the total 2,3,7,8-TCDD concentration, can be found in Rao *et al.*⁷. The uncertainty, in terms of a 95% confidence interval for the annual mean dioxin concentration, due to the presence of **both** the values below the LOD and the natural variability of atmospheric concentration data is determined from Equation 2, and the results are presented in Table II. In general, there is excellent agreement between the upper 95% confidence bounds for the annual mean concentration determined using the uniform and normal assumptions for the data in the region below the LOD. The annual mean dioxin concentrations from these approaches are also in reasonable agreement with that determined from the bootstrap method.

We invoked the central limit theorem in determining the 95% confidence intervals for the mean concentration from the uniform and the normal fill-in approaches. In the bootstrap method, we entered the original sample only once to draw concentrations in the region below the LOD to reconstruct the original sample. Hence, the outcome of this approach is strongly dependent upon the net concentration values in the reconstructed original sample. A more computer-intensive approach to alleviate this limitation is to repeatedly, say 100 times, enter the original sample containing the values below the LOD to reconstruct the original sample, and subject each reconstructed sample to 100 bootstrap replications to calculate the mean. Then, the **medians** for the 2.5%, 50% and 97.5% values can be determined from the cumulative frequency distributions of the means to construct the 95% confidence bounds for the mean concentration. The upper 95% confidence bounds for the annual mean dioxin concentration, estimated from this intensive computation procedure, are 0.460, 0.323, and 0.283 pg/m³ for the three data subsets shown in Table II, each covering a one-year sampling period. The upper 95% confidence

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Table I

Concentrations of PAHs in NIST Standard Reference Materials
Determined Using SFE and SFE-GC

	<u>Concentration: certified value/SFE value (ug/g)*</u>		
	marine sed. (SRM 1941)	urban dust (SRM 1649)	diesel part. (SRM 1650)
fluoranthene	1.22/1.45	7.1/7.3	51/53
benz[a]anthracene	0.55/0.60	2.6/2.6	48/47
benzo[a]pyrene	not reported	2.9/2.8	1.2/1.4
indeno[1,2,3-cd]- pyrene	0.57/0.56	3.3/3.0	not reported

*The certified value is given first followed by the concentration determined using SFE (for SRM 1650) or SFE-GC/MS (for SRMs 1941 and 1649). SFE extractions for SRMs 1941, 1649, and 1650 were (respectively) 10 minutes with N₂O, 15 minutes with N₂O, and 30 minutes with CO₂. See references 1,2,4, and 6 for details.

bounds estimated from the Monte Carlo uniform fill-in approach compare favorably to these estimates from the more computer-intensive approach.

Conclusions

We presented several methodologies to quantify the inherent uncertainty due to the presence of values below the LOD in the data set and the natural variability of the atmospheric concentration data. The analysis methods discussed here are able to estimate the mean concentration of the pollutant reasonably well, but the results indicate that the 95% confidence limits for the mean are sensitive to the assumptions invoked regarding the nature of the underlying data. Although the bootstrap method, as applied here, does not require the determination of the true distribution of the data, the results may be sensitive to the procedure used for reconstructing the original sample.

The upper 95% confidence bound for the annual mean may be more appropriate in exposure assessment and risk analysis, because this higher limit allows us to make conservative estimates of the risk associated with the human exposure to toxic air contaminants. If the distribution of the original data is not known *a priori*, one may have no choice except to assume that all values between zero and the reported LOD are equally likely to occur, or to apply distribution-free techniques. Under these conditions, the results from this study suggest that the assumption of uniform distribution to fill-in for the values below the LOD, followed by the Monte Carlo simulation procedure, is a reasonable methodology for estimating the upper 95% confidence bound for the mean concentration.

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TABLE I. Comparison of the **medians** of the means and standard deviations, and the 95% confidence intervals for the means, for different “fill-in” methods for the hypothetical data set of sample size 60 drawn from $N(20,5)$.

Scenario	Mean	Standard deviation	95% Confidence interval
Original sample	19.941	4.505	18.772 to 21.110 18.523 to 20.773*
<u>Censoring at the 10th percentile</u>			
<LOD \equiv 0.5 LOD	19.930	4.488	-
Uniform	19.921	4.532	18.745 to 21.097
Normal	19.925	4.497	18.758 to 21.092
Bootstrap	19.915	4.390	18.371 to 21.028
<u>Censoring at the 50th percentile</u>			
<LOD \equiv 0.5 LOD	19.031	4.948	-
Uniform	19.048	5.324	17.666 to 20.430
Normal	19.037	5.027	17.733 to 20.341
Bootstrap	19.678	4.861	18.239 to 20.840

*Determined from the bootstrap method.

TABLE II. Annual mean concentration and its 95% confidence interval for the dioxin data collected in Niagara Falls, NY, during September 1986 to March 1988.

Data subset	Approach	Annual mean concentration (pg/m ³)	95% Confidence interval (pg/m ³)
Sept 1986 to Aug 1987 (Sample size = 24)	<LOD \equiv 0	0.306	-
	<LOD \equiv 0.5 LOD	0.382	-
	<LOD \equiv LOD	0.458	-
	Uniform	0.381	0.311 to 0.452
	Normal	0.382	0.312 to 0.452
	Bootstrap	0.374	0.184 to 0.636
Jan 1987 to Dec 1987 (Sample size = 26)	<LOD \equiv 0	0.169	-
	<LOD \equiv 0.5 LOD	0.277	-
	<LOD \equiv LOD	0.385	-
	Uniform	0.261	0.218 to 0.304
	Normal	0.260	0.217 to 0.303
	Bootstrap	0.262	0.159 to 0.363
Apr 1987 to Mar 1988 (Sample size = 27)	<LOD \equiv 0	0.130	-
	<LOD \equiv 0.5 LOD	0.236	-
	<LOD \equiv LOD	0.342	-
	Uniform	0.235	0.197 to 0.273
	Normal	0.236	0.197 to 0.275
	Bootstrap	0.225	0.156 to 0.319

USE OF THE SURFACE ISOLATION FLUX CHAMBER TO ASSESS FUGITIVE
EMISSIONS FROM A FIXED-ROOF ON AN OIL-WATER SEPARATOR FACILITY

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The release of fugitive volatile organic compound (VOC) emissions from an oil-water separator facility at a refinery was studied. The first phase of the testing was a screening of all sources of hydrocarbon emissions on the fixed roof of the separator. These sources included seams in the cement roof and covered observation ports. All seams were tested and categorized into a characteristic range of VOC source. It was then possible to express the fugitive VOC emissions from the seams in terms of number of lineal feet of roof seam per class of seam (e.g., 125 feet of seam, range 0 to 10 ppmv VOC etc.) Likewise, all ports were surveyed and categorized in a similar fashion.

After all sources of VOCs were surveyed and categorized, representative sources from each category (seams and observation ports) were studied using an emission isolation flux chamber to determine the emission rate of VOCs from the facility. This approach was cost-effective since a minimum number of emission measurements were performed. In this way, a correlation between the onsite TNMHC and hydrocarbon speciation data was made.

Total TNMHC emissions were calculated by summing the emissions from all categories of seams and all categories of ports and expressing the fugitive emissions as TNMHC emissions from the roof on the facility.

Introduction

Radian Corporation performed testing of fugitive total non-methane hydrocarbon emissions from a fixed-roof oil/water separator designed by the American Petroleum Institute (API) at a refinery in California. The refinery was required to demonstrate that the control measures placed on the separator were effective at controlling fugitive emissions to the acceptance of the local air quality management district agency. The EPA recommended surface emissions isolation flux chamber was used to measure the emissions from the API separator. Although not specifically intended for this purpose, the direct measurement approach using the flux chamber provided to be an effective measurement approach for this fugitive source. These data were then used to demonstrate effective control of VOC emissions by the fixed-roof. As such, this paper will focus on the application of this emission assessment technology to this unique VOC emission source.

Facility Description

The fixed-roof separator involved in the program was an experimental model that was constructed and tested to satisfy a local air district control requirement. The design of the separator was unique in that the fixed-roof construction was intended to contain all fugitive emissions from the oil waste. The features of concern for the fugitive emissions testing program were the seams in the roof and the observation ports.

The separator consisted of two cells each having an outside dimension of about 22 feet by 174 feet. The roof was constructed of metal I-beams and concrete slabs. The unique feature of the roof design was a compression gasket placed between the metal beams and the concrete slabs. Each cell of the separator had a total of thirty, 4 feet by 21 feet slabs that covered the main area of each cell. These slabs were fastened to the metal beam structure but the slabs were not united in any way. They were, however, sealed with a caulk material. In fact, the cell that was tested had four types of caulk material that was being evaluated for effectiveness (hard rubber, soft rubber, metal tape, and cement).

In addition to the slab seams, there were a total of six observation ports having a dimension of 1 foot by 3 foot. Each port had a lid and a rubber gasket to seal the lid to the roof port. These lids were not air-tight and later proved to be a primary source of fugitive emissions, as did those seams that had weathered or incomplete caulk. There was no active control technology on these units and the waste streams were not treated in any way upstream of the separators. The concept of this design was to seal the separator with a fixed-roof and prevent fugitive emissions by using a "leak-tight" roof. No attempt was made to limit the head space air volume and there was no concern of explosion hazard.

Summary of the VOC Testing Program

There are several ways in which to assess the fugitive emissions from a facility such as the separator. One class of technologies that could be used are indirect emission measurement technologies. These technologies involve the collection of ambient air samples downwind of the facility (or source) and rely on dispersion modeling to estimate a source term that could have generated those measured downwind concentrations. Normally, indirect assessment technologies are preferred for situations like this one where the emissions are from many fugitive sources that collectively act as a heterogeneous area source. However, the disadvantages of the indirect approach outweighs the advantages. Indirect technologies are subject to upwind interferences which can be significant at a refinery, especially when the same or similar compounds can be found upwind as well as downwind of the source being tested. Another significant disadvantage is that the downwind concentrations will be low if the source has a low emission rate, which is the case here. Lastly, indirect technologies are governed by the dispersion of air contaminants at the facility. The efficiency of collecting data and the quality of the data are controlled by parameters that the scientists has no control over. For these reasons, the testing approach selected was from the class of technologies known as direct emission assessment technologies.

The testing approach for assessing the VOC emissions from the separator employed field screening and direct emission measurements using the Surface Isolation Emission Flux Chamber.¹ This direct emissions measurement technology was developed for EPA by Radian Corporation and is now a recommended technology for measuring emission rates from fugitive area sources. The primary advantage of using this technology is that the emission rate is calculated from measured parameters, all of which the scientist has control over. The technology is free from upwind interferences, and is applicable to a variety of surfaces including emissions from cracks, vents, and fugitive emissions from observation ports. The disadvantage is that the entire source must be assessed and that means that the source must be understood and then representatively tested.

The emissions testing program consisted of screening to select representative sampling locations and emission measurements that could be summed in order to calculate an emission rate of VOC's from the facility. Preliminary screening indicated that the majority of fugitive emissions were from the caulked seams in the cement slab construction and from the observation ports throughout the roof. The screening activities using real-time analyzers indicated that there were 20 categories of seams that required testing: 4 types of caulk material; and 5 ranges of VOC concentration above the caulked seams. The seam length per each type of seam caulk was measured and representative emission rate measurements were made using the isolation emission flux chamber where needed to satisfy the screening data needs. Not all types of seam caulk had VOC concentration measurements in each of the five concentration ranges identified and flux chamber measurements were not

required for all 20 categories.

The results of the seam testing by category were used to calculate the total non-methane hydrocarbon (TNMHC) fugitive emissions by multiplying the unit emission rate data per category of seam by the lineal feet of each category of seam and summing these data to obtain the TNMHC emissions for caulked seams on the separator cell (Table 1). It was estimated that the TNMHC fugitive emissions from the seams was 0.56 pounds per day calibrated as hexane. In addition, testing was conducted on ports with the lids open and closed, and with lids with and without over gaskets of rubber. It was found that a metal lid controls emissions about 44 percent and 80 percent with an additional gasket.

The same approach was used for the observation ports; screening with real-time analyzers and the flux chamber measurements over the covered ports to estimate the fugitive emissions from this source (Table 2). In the same way, an estimate of TNMHC fugitive emissions of 0.34 pounds per day calibrated as hexane was made for all six observation ports per cell.

Considering that the total fugitive emissions for TNMHC were believed to come from the caulked seams and the observation ports, the total emissions estimate for the separator cell was 0.90 pounds per day calibrated as hexane.

The effectiveness of the fixed-roof control measure was assessed by summing the fugitive emission sources and dividing by the estimated, uncontrolled emission rate estimate derived by the Litchfield equation. The control efficiency of the fixed-roof was estimated to be 98 percent.

Summary and Conclusions

The primary conclusions from this testing and research effort are as follows:

- o The fugitive TNMHC emissions from a fixed-roof API oil/water separator on the day of testing were measured and found to be 0.90 pounds per day as hexane.
- o The overall control efficiency of the fixed-roof on the separator without waste pre-treatment or an additional control technology was estimated at 98 percent.
- o Additional controls consisting of over gaskets on ports and flexible continuous caulking in seams can improve the control efficiency of fugitive emissions from fixed-roofs on separators.
- o If used with a screening technology, the direct measurement technologies can be effective in assessing fugitive emissions from these types of fugitive emission sources.

TABLE 1. RESULTS OF DIRECT EMISSIONS TESTING OF SEAMS

SEAM EMISSIONS: EMISSION RATE PER CATEGORY OF OVA CONCENTRATION (ppmv) as lbs hexane/foot-day

TYPE	< 10 ppmv OVA	10 - 50 ppmv OVA	50 - 200 ppmv OVA	200 - 1,000 ppmv OVA	>1,000 PPMV OVA
HARD RUBBER	590' @ 1.6E^{-5}	23' @ 9.0E^{-4}	18' @ 6.9E^{-3}	5' @ 5.5E^{-2}	NA
SOFT RUBBER	236' @ 1.0E^{-5}	3' @ 9.0E^{-4}	1.3 @ 1.9E^{-2}	NA	NA
METAL TAPE	233' @ 6.5E^{-5}	5' @ 9.0E^{-4}	3' @ 1.5E^{-3}	1.3 @ 5.5E^{-2}	NA
CEMENT	62' @ 1.4E^{-5}	NA	NA	NA	NA

TOTAL EMISSIONS FROM SEAMS: 0.56 lbs/day as hexane.

NA - NOT APPLICABLE

TABLE 2. RESULTS OF DIRECT EMISSIONS TESTING OF PORTS

PORT EMISSIONS: EMISSION RATE PER CATEGORY OF OVA CONCENTRATION (ppmv) as lbs. hexane/port-day

TYPE	NUMBER	OVA SCREEN (ppmv)	EMISSION RATE (lbs. hexane/port-day)
INLET PORT	4	1,000 - 2,000	6.8E^{-2}
OUTLET PORT	2	6,000 - 7,000	4.9E^{-2}
PUMP PORT	2	NOT TESTED	4.9E^{-3}

TOTAL EMISSIONS FROM PORTS: 0.34 lbs./day as hexane

AN ATTEMPT TO MEASURE THE AIR TOXICS IMPACTS OF THE GREATER DETROIT RESOURCE RECOVERY FACILITY

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INTRODUCTION

An intensive ambient air monitoring program was initiated in January 1988 in the vicinity of the Greater Detroit Resource Recovery Authority's (GDRRA) resource recovery facility located in Detroit, Michigan. In July 1989 the facility finished initial compliance testing and began commercial operation. The facility is designed to receive and process a maximum of 4000 tons/day of municipal solid waste (MSW). Typically, the processing equipment will shred, screen and magnetically separate 3300 tons of solid waste to produce refuse derived fuel (RDF) five days a week. Each day, seven days a week, up to 2400 tons of RDF can be used as boiler fuel for production of steam and electricity.

The ambient air monitoring program being conducted by Roy F. Weston, Inc. (WESTON) for GDRRA began in January 1988. The objectives of the air monitoring program are to:

- Document the background levels of the pollutants of concern that will be emitted from the waste-to-energy facility.
- Gather sufficient data to determine the actual ambient impact of the GDRRA facility emissions.

WESTON established and operates ambient air monitoring equipment at two sites in the vicinity of the GDRRA facility. One of the monitoring stations, the "Playground Site", is located near the predicted location of the maximum annual ground-level concentration and annual maximum dry pollutant deposition. The second site used by WESTON, the "Wayne County Site", was selected as representative of the regional background air quality beyond any significant influence of the resource recovery facility. In addition to the two sites operated by WESTON, Environment Canada operates two monitoring stations in the Windsor, Ontario area that provide data of potential use in WESTON's air quality impact analysis.

The pollutants of concern include trace metals, organic compounds (which could result from incomplete combustion of the MSW), acid gases and inhalable particulate matter. The organic compounds being sampled and analyzed include dioxins, furans, PCB's, polynuclear aromatic hydrocarbons, chlorobenzenes and chlorophenols. The metals being analyzed include lead, copper, zinc, mercury, nickel, manganese, arsenic, chromium, vanadium, selenium, cadmium and antimony.

The first phase of the ambient air monitoring program was designed to gather background air quality data for at least one year prior to the start-up of the GDRRA facility. The monitoring program will continue for at least one year after the GDRRA facility begins operation to determine if measurable air quality impacts occur.

The design of the ambient air toxics monitoring program was coordinated with an ad-hoc interagency committee of the federal, state, provincial and local air pollution control agencies in the Detroit-Windsor area.

SAMPLING SITES

Ambient air quality data is collected by WESTON for the GDRRA at two monitoring stations in Detroit. The "Playground Site" is located at the Grandy Street/Medbury Street Playground, which is predicted by air quality modeling to be in the area of the maximum air quality impacts from the GDRRA facility. The Playground Site is located approximately 0.65 miles northeast of the GDRRA facility.

The second monitoring station operated by WESTON is called the "Wayne County Site". This site, which is located near the Southeastern High School on Goethe Street, was selected as representative of the regional background level concentrations for the pollutants of concern. The Wayne County monitoring station is located approximately 3.8 miles east of the GDRRA facility. The Wayne County Site is being considered a background site in the sense that it is anticipated to be much less influenced by the emissions from the GDRRA facility relative to the Playground Site.

In addition to the two monitoring stations operated by WESTON for GDRRA, Environment Canada operates two air quality monitoring stations in areas potentially impacted by the GDRRA facility, but to a much lesser degree than the Detroit Playground Site. The two Environment Canada sites are referred to as the Windsor Site and the Walpole Island Site. The Windsor Site is located approximately four miles south of the GDRRA facility in Windsor, Ontario. Environment Canada began sampling at the Windsor Site in July 1987. In January 1988, they began sampling at the Walpole Island site which is located approximately 35 miles to the northeast of the GDRRA facility. The Walpole Island Site is considered representative of a remote background site.

SUMMARY OF SAMPLING AND ANALYTICAL METHODS

The pollutants of concern and the sampling methods and analytical procedures are described below. This is the first time an attempt has been made to identify and quantify most of these pollutants in Detroit.

Pollutants of Concern

While there are many pollutants of concern in ambient air, this study focuses on those pollutants that are specifically thought to be associated with the combustion of municipal solid waste. Table 1 provides a list of pollutants that are included in the monitoring study. Table 2 provides a list of the semi-volatile organics analyzed for in the PAH and PCB, chlorobenzene, chlorophenol samples. Many of these pollutants may be emitted from resource recovery facilities. They have been classified as pollutants of concern in previous health risk studies. The pollutants of concern are compounds or elements, which potentially contribute to long-term, chronic health effects. While

some of these compounds also have short-term, acute health effects, there are no conceivable plant operating conditions that could lead to an exceedance of accepted short-term standards or criteria nor any long-term or chronic exposure criteria. Although none of the many studies that have been conducted concerning waste-to-energy facilities have identified any potential health impacts, this study is being conducted to confirm such results.

Sampling and Analytical Methods

The sampling and analytical methods employed by WESTON are identified in Table 3. The selected sampling and analytical methods are published EPA and NIOSH methods. In general, these are the same methods used by Environment Canada in their air quality monitoring program at the Windsor and Walpole Island Sites. This was an important point in method selection. The use of the same or very similar sampling and analytical methods will enable the monitoring results from both the Michigan and Ontario sides of the Detroit River to be merged into a single database to determine the relative air quality impact of the GDRRA facility.

The detection limits for the pollutants of concern are also noted in Table 3. The detection limits for dioxins and furans are in the 0.05 to 0.5 picograms per cubic meter range (10^{-12} grams/ m^3) depending upon the species of dioxin or furan being measured. The detection limit for PCB's and chlorobenzenes and chlorophenols are approximately 2 to 20 pg/ m^3 . The detection limits for the other organics and trace metals are in the nano-grams per cubic meter range (10^{-9} grams/ m^3).

Sampling Schedule and Period

PAH, metals and acids samples are collected at both WESTON sites every six days. PCB's and chlorobenzenes and chlorophenols are sampled every twelve days. Dioxins and furans are sampled every 24 days. To collect a sufficient air sample volume to obtain the desired detection limits for dioxin/furans, PAH's, PCB's, CLB and CLP, WESTON samplers are operated for 48 hours. The samples for the other pollutants of concern are collected over 24 hour periods by WESTON. The 48-hour samples are collected from noon to noon.

Methods For Identifying Ambient Air Quality Impacts

Several methods are planned to identify and characterize the air toxics impact using the pre- and post- operation ambient data. A preliminary evaluation has been performed each quarter since the beginning of the sampling activities. Each calendar quarter the air sampling, meteorological and boiler operations data are tabulated and entered into a database. Quarterly data reports are prepared which present tabulated and graphical (bar chart) summaries of the mean values, standard deviations, maximum values and number of values above the detection limits. The quarterly summaries have been compared visually or "by-eye" against previous quarterly summaries to flag trends or obvious impacts. To date no significant air toxics impacts have been

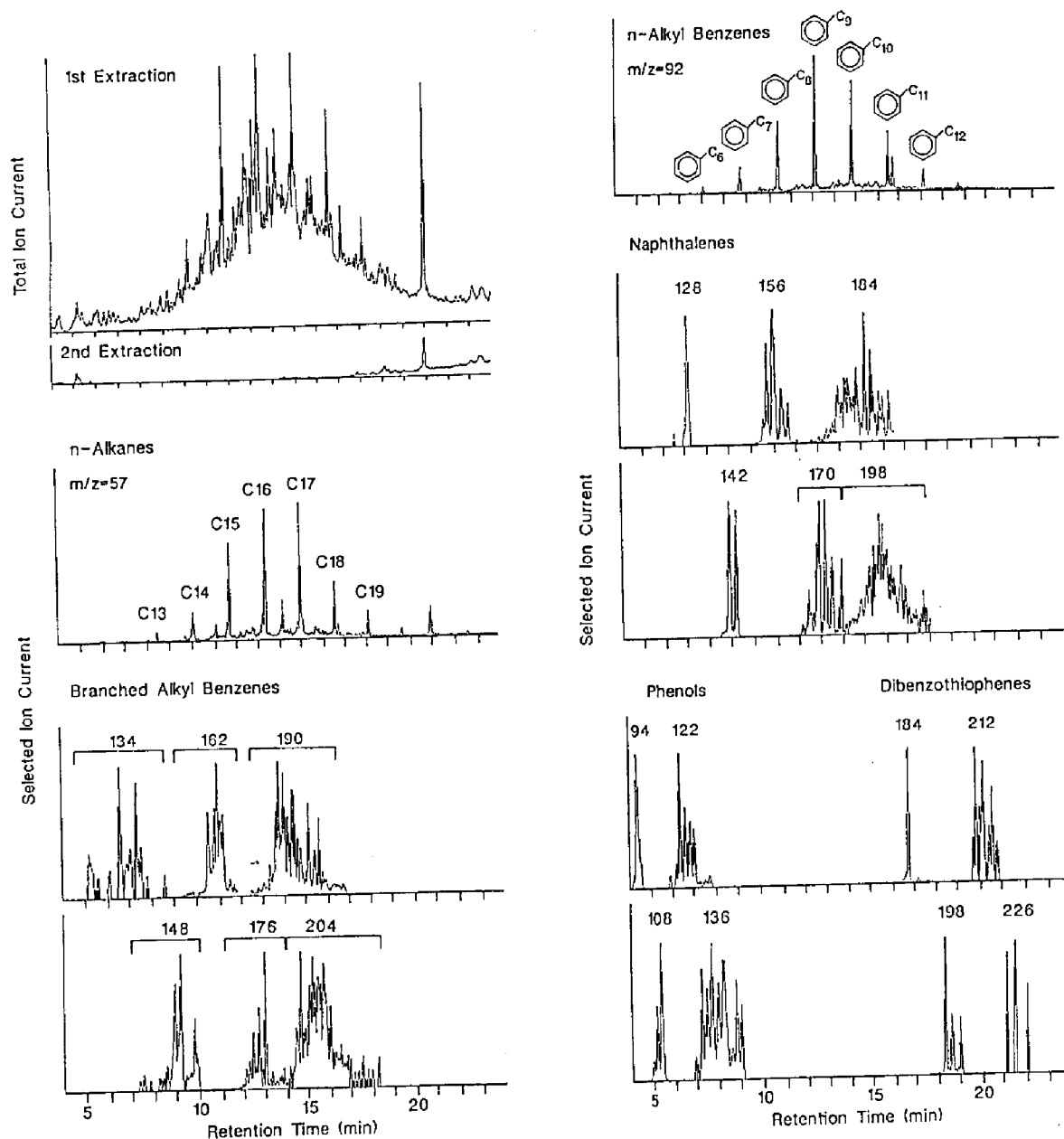


Figure 1. SFE-GC/MS analysis of roofing tar volatiles collected near the tar vat operator's face. The entire analysis including sample collection (10 minutes), supercritical fluid extraction (10 minutes), and GC/MS analysis (except data reduction) required <1 hour. The numbers above the selected ion plots indicate the mass of the selected ion plot. See reference 5 for details.

observed and the facility does not appear to be increasing ambient air toxic concentrations above existing pre-operational levels.

Only preliminary analysis and interpretation of the data have been accomplished to date and the collection of post operation ambient data is ongoing. During the first half of 1989 the facility was undergoing start-up activities and hence the combustion of RDF was intermittent and quite variable. The summer season (July through September) of 1989 was the first quarter in which the facility operated in a routine manner, although RDF combustion at the design rate was seldom achieved. Since completing start-up the facility has typically operated with only one boiler and only about 1000 TPD of RDF has been combusted.

The summer season of 1989 has been compared to the summer of 1988. A series of barcharts provides a side-by-side comparison of the seasonal data from the two years. These figures are included as an appendix to this paper. This simplistic type of comparison identifies no air toxics impact from the facility. It appears that the emissions from the facility have little or no measurable ambient air toxics impact. For most of the pollutants included in the study, the ambient concentrations actually decreased in 1989. Meteorology must be considered and a larger database with more seasons of sampling are needed before any conclusions can be made.

Other methods will be used to investigate potential impacts. Dispersion modeling will be performed to study specific sampling days to compare the predicted air quality impacts from the air toxic emissions from the facility to the actual measured ambient concentrations. Meteorological data are continuously gathered at the Playground monitoring station and records are kept of the rate of RDF combustion in each boiler and per day. Emission test results are also available from the initial compliance test program to relate pollutant emissions to the quantity of RDF combusted. Days with prevailing winds that would carry the plume towards one of the monitoring stations can be studied and comparisons of predicted air toxic impacts to measured ambient concentrations can be performed.

When approximately one year of post-operation data are available, a comprehensive statistical analysis of the database is planned. Multi-variate analysis of variance will be used to determine if measurable air toxic impacts have occurred. Each pollutant emitted from the facility can be evaluated and these results for different pollutants compared. The large number of variables, in particular, meteorological factors (such as wind speed, direction, atmospheric stability, etc.) which may vary significantly during most sampling days and from one sample day to the next are expected to make this statistical analysis quite difficult. Further complicating this analysis is the variability in pollutant emission rates which vary from day to day (and hour to hour) depending on boiler operation and RDF combustion rates.

TABLE 1

LIST OF POLLUTANTS THAT ARE INCLUDED
IN THE GDRRA MONITORING STUDY

EMISSION	SYMBOL	REASON FOR SAMPLING
<u>Dioxins and Furans</u>		
Polychlorinated dibenzo-p-dioxins and Polychlorinated dibenzofurans	PCDD, PCDF	a, d
<u>Semi-Volatile Organics</u>		
Polynuclear Aromatic Hydrocarbons	PAH	a, d
Polychlorinated Biphenyls	PCB	a, d
Chlorobenzenes and Chlorophenols	CLB, CLP	
<u>Trace Metals</u>		
Antimony	Sb	a, d
Arsenic	As	a, d
Cadmium	Cd	a, d
Chromium	Cr	a, d
Copper	Cu	a, d
Lead	Pb	a, b, c, d
Manganese	Mn	d
Mercury	Hg	a, c, d
Nickel	Ni	a, d
Selenium	Se	d
Vanadium	V	d
Zinc	Zn	d
<u>Inhalable Particulate Matter</u>		
Inhalable Particulates	PM10	a, b, d
<u>Acid Gases</u>		
Hydrogen Chloride and Inorganic Acids	HCl	a

- a Generally recognized pollutant emission from resource recovery facilities
 b Federally-regulated: "criteria pollutant."
 c Federally-regulated: "PSD pollutant".
 d Emission of concern from a standpoint of high toxicity, and/or high inhalable particle concentration.

TABLE 2

SEMI-VOLATILE ORGANIC MEASUREMENTS

POLYNUCLEAR AROMATIC HYDROCARBONS (PAHs)

Acenaphthylene	Benzo(a)anthracene
Acenaphthene	Benzo(b,k)fluoranthene
Fluorene	Benzo(a)pyrene
Phenanthrene	Indeno(1,2,3-cd) pyrene
Anthracene	Dibenz(a,h)anthracene
Fluoranthene	Benzo(g,h,i)perylene
Pyrene	
Chrysene	

POLYCHLORINATED BIPHENYLS (PCBs)

10 Isomer Groups

CHLOROBENZENES (CLB)

Trichlorobenzene
 Tetrachlorobenzene
 Pentachlorobenzene
 Hexachlorobenzene

CHLOROPHENOLS (CLP)

Dichlorobenzene
 Trichlorophenol
 Tetrachlorophenol
 Penta chlorophenol

TABLE 3

AMBIENT MONITORING METHODS AND DETECTION LIMITS

COMPOUND	SAMPLING METHOD	ANALYTICAL METHOD	SAMPLE VOLUME	TARGET DETECTION LEVEL	SAMPLING EQUIPMENT
Dioxin/Furan	Hi-Vol/PUF	GC-MS (8280)	800 m ³	0.05 - 0.5 pg/m ³	General Metal Works PS-1
PCB	Hi-Vol/PUF	GC-MS	800 m ³	2 - 20 pg/m ³	General Metal Works PS-1
Chlorobenzenes	Hi-Vol/PUF	GC-MS	800 m ³	10 pg/m ³	General Metal Works PS-1
Chlorophenols	Hi-Vol/PUF	GC-MS	800 m ³	10 pg/m ³	General Metal Works PS-1
PAH	Hi-Vol/PUF-XAD	GC-MS-SIM	700 m ³	0.02 - 0.2 ng/m ³	General Metal Works PS-1
Particulates (PM10)	Med-Flow	Gravimetric	160 m ³	---	Sierra Anderson Medium Flow
Metals	Med-Flow-TFE	XRF	160 m ³	0.09 - 9 ng/m ³	Sierra Anderson Medium Flow
Inorganic Acids	NIOSH 7903	IC Scan	0.5 m ³	2 - 10 ug/m ³	Silica gel tube
VOC	EPA TO-14	GC-MS	16 L	0.1 ug/m ³	Evacuated Canister

EMISSION OF OZONE AND DUST
FROM LASERPRINTERS.
PRESENTATION OF A NEW
EMISSION SOURCE TEST METHOD.

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Abstract

A new method has been developed to measure emissions from office equipment to provide figures for the contribution to local indoor air pollution from different sources e.g. laser printers.

The tests are conducted in a climatized room. The total air emissions from the equipment, e.g. a printer is collected in a funnel, the equipment is tested for leaks, the total air flow is measured, the concentration of ozone and particles in the outlet air is determined, and the results are given as micrograms pr. minute of ozone and dust. As the results are given as a single number for each tested item the method also gives the possibility for ranking between printers for the tested component.

The average emission of ozone from printers without filter is 440 $\mu\text{g}/\text{min}$ for printers. With built-in filters the average emission is 100 $\mu\text{g}/\text{min}$. It is shown that these emissions will give significant contributions to exposure concentrations in an office.

Introduction

Installation of personal office equipment in poor ventilated small offices is often seen to cause unacceptable indoor air pollution. The nuisance from office equipment is often complex and can be described as a combination of draw, elevated temperatures, dust from printers, and ozone generated from corona discharges in laser printers and photocopying machines.

Sources to indoor ozone exposure

Ambient air is the common source of indoor ozone. The concentration is varying in time and by place. The indoor concentration level from this source is determined by the actual ambient levels, reduction in the air conditioning system, and air exchange rate. It is also known from the literature that electrostatic filters, photocopying machines, laser printers and other equipment with electric discharging generate and emit ozone /1/.

Printer technology

The principles of the laser printer technology are shown in Figure 1. The formation of ozone takes place in an electric field (AC or DC) between the corona wire (DC, positive or negative) and a photosensitive surface on the "image drum".

The generation of ozone from atmospheric oxygen in this field depends on the field type and the field strength, which is related to the distance from the corona wire to the photosensitive surface. The generated ozone will decompose by catalytic reactions at surfaces. In a number of printers this decomposition is enhanced by high temperature, a long residence time and a built-in filter.

Equipment and ventilation of the modern office

During the last 5 - 10 years we have seen the introduction of personal computers, computer networks and local laser printers into the modern office. This development has introduced new relative large sources of ozone and heat into the office. The contribution from ambient ozone to indoor ozone levels is much lower in Denmark than in e.g. metropolitan areas in the United States.

Many Danish office buildings have ventilation systems which are unable to meet the requirements needed to secure acceptable low ozone concentrations and temperature.

Definitions and principles

The emission of ozone/dust is defined as the total amount of ozone/dust leaving the printer pr. minute. This definition allows for catalytic decomposition of ozone and deposition of dust inside the printer. The definition means that the emission includes point sources and diffuse sources.

To collect all air streams from the printer it is equipped with a funnel. Diffuse sources and leaks are sealed with film and tape (Figure 2) and checked by leak testing for ozone. The airflow rate through the funnel and the concentration of ozone and dust are determined.

To make comparable results the printer is set to produce standard test prints at maximum printing rate on standard 80 g/m² paper, and the tests are performed in a test room with controlled temperature, humidity and ozone (20°C, 50% relative humidity, < 0.001 ppm respectively).

Every test includes two independent tests with replacement of the funnel between the tests.

The emission of particulate matter from the printer is of primary relevance for the deposition inside the printer or on the built-in filter, where deposition of particulate matter increases the pressure loss over the filter and will contribute to catalytic destruction of ozone.

Experimental

Air volume flow rate: The air velocity v (m/s) is determined with a calibrated spinwheel anemometer (Lambrecht) as the mean of 3 repeated 1 minute average values for each independent test. The area of the funnel opening is A (m²), and the air volume flow rate Q (m³/h) is calculated as:

$$Q(\text{m}^3/\text{h}) = v(\text{m/s}) * A(\text{m}^2) * 3600(\text{s/h})$$

Air volume flow rates are reported at standard conditions (20°C and 1 atm.).

Determination of ozone concentration: A conventional ozone monitor (AID 560) based on the chemiluminiscence principle is used for determination of the ozone concentration C (ppm) in the funnel opening cross section. To avoid errors from non-uniform distribution over the cross section the teflon sample probe is traversed. Before each test the ozone monitor is calibrated using the AID 565 ozone generator, which is calibrated at regulary intervals against a standard iodometric method /2/.

The range for the actual instrument is 0.001 - 10 ppm ozone.

The ozone emission concentration (E) is determined as the average of 3 repeated 1 minute average values of the 2 independent tests. The results are read from the instrument display.

The emission of ozone E(microgram/min) at 20° C is calculated as:

$$E(\mu\text{g ozone/min}) = C(\text{ppm}) * 1995 \mu\text{g/m}^3/\text{ppm} * Q(\text{m}^3/\text{h})/60 (\text{min/h})$$

Determination of particle emission: From the funnel a representative sample of air is taken isokinetical through a 37 mm pre-weighed membrane filter (Millipore AA, 0.8 μm). The sample time is 60 min. The air wolume is determined by a calibrated gas meter.

The amount of dust sampled on the filter is determined gravimetrically with a microbalance (Cahn 25) at controlled air conditions (20°C and 50 % relative humidity). Detection limit < 0.01 mg/m³.

As a standard routine the composition of the dust is characterised by optical microscopy.

Results

During the last 5 years our Institute has tested approx. 40 different printers. All printers have been tested without a built-in ozone reduction filter, and 50% of these have been tested with an internal ozone reduction filter. In addition to this our Institute has performed tests to describe the ozone reduction for new and aged filters. The tests have been performed for producers and suppliers to the Danish market, and results for individual printers and external filters can be obtained from the relevant supplier or producer of the printer.

Test results are shown on the Figures 3 - 6 for ozone and Figure 7 for particle emissions.

Table I gives a summary of the obtained results.

Ozone emission from printers without built-in filter

It is possible technically to reduce the ozone production rate without the use of filters, e.g. by improved principles for the electrostatic proces.

Ozone emission reduction by built-in filters

The reduction efficiency is defined as:

$$R = (1 - E(\text{with filter})/E(\text{without filter})) * 100 \%$$

E(with filter) and E(without filter) measured at identical test conditions, paper quality and printer settings etc.

For the tested printers the ozone reduction varies from 10 to 90%. The sources of variation in the ozone reduction are:

- type of filter (corrugated paper or PUR-foam impregnated with activated charcoal or an activated charcoal grid)
- leakages caused by incorrect or inexpedient mounting of filter
- increased catalytic reduction of ozone caused by longer air residence time inside the printer

We have not performed tests to quantify sources of variations in ozone reduction efficiency. The obtained maximum reduction efficiency of 90% can be obtained when the development, production, installation and operation of printers are performed according to accepted rules for quality control. This reduction efficiency can be increased by further development of the internal filters in the different printers. No apparent or statistical significant connection between any of the factors emission of particulates, the ozone emission or the ozone emission reduction can be seen.

Ozone emission reduction by external filters

For the different types of external filters on the Danish market the ozone reduction efficiency has been tested in

connection with different printers from different suppliers. For new filters, correctly installed etc. the ozone emission concentration is at or below the detection limit of the instrument, which gives an emission reduction efficiency beyond 99.9 %.

Discussion

The test method described is shown to give results that provide us with information on the ozone emission from laser printers and the methods used to reduce the ozone emission from these printers. The information on emission levels can ranking of printers according to their emission and for predicting exposure levels for different categories of printers.

Emission reduction:

It is important to notice that with the current used filters we have experienced a rapid decrease in the reduction efficiency of these filters due to particular deposition on the filters. Higher average values will then develop with time.

The emission source test method has been used actively in Denmark for the development of active external filters based on the principle of a prefilter for particulants followed by granulated active carbon. This technology effectively removes dust and ozone, and the ozone reduction efficiency does not decrease as rapidly as for other filter types.

Exposure levels for ozone in offices:

In Denmark regulations of ozone emission and exposure are limited to 100 ppb for industrial work-exposure. For indoor exposure in offices there is no exposure limit.

Based on the test results of ozone production from the laser printers and the common model for calculation of average concentrations in rooms with known ventilation rate, volume, inlet concentration of ozone, rate constant for surface catalyzed decomposition average concentrations can be calculated.

The results are shown in Table 2 for one example and for different printer categories and printing rates. These results are also shown on Figure 8.

The equilibrium concentrations obtained by this simple box-model will give average values for the concentration of ozone in the room or in a part of a room confined by thermal movements in the room.

Although equilibrium concentrations are often used for regulatory purposes, problems are experienced at concentrations well below the threshold limit value. In situations where a confined plume from the printer points towards a person, the concentration of ozone in the breathing zone will often be higher depending on the initial concentration and the dilution by distance and thermal movements. Consequently such a person might be effected by the ozone.

References

1. B. Andersen, T.B. Hansen, "Ozone and other Air Pollutants from Photocopying Machines", Am. Ind. Hyg. Assoc. J. 47: 659 (1986).
2. "Ozone in Air method", NIOSH, P&CAM. 154.

Table I.

Summary of test results

	Without filter	With filter
	Avg.+/-St.dev.	Avg.+/-St.dev.
Ozone $\mu\text{g}/\text{min.}$	438+/-277	102+/-98
Ozone conc., ppb	504+/-290	--
Particulates $\mu\text{g}/\text{min.}$	--	61+/-74*

* Note: Particulate emission data not normal distributed

Table II.

Ozone equilibrium conc. (in ppb) at different printing rates.

Printer category	Printing rate		
	100 %	50 %	10 %
Worst case	380	190	39
Average	135	68	14
Low	30	15	3
Minimum	background/other sources		

Note: ventilation rate q (1 pr. hour), volume v (25 m^3), inlet concentration of ozone C_0 , rate constant for surface catalyzed decomposition k ($0,05 \text{ min.}^{-1}$) average concentrations can be calculated.

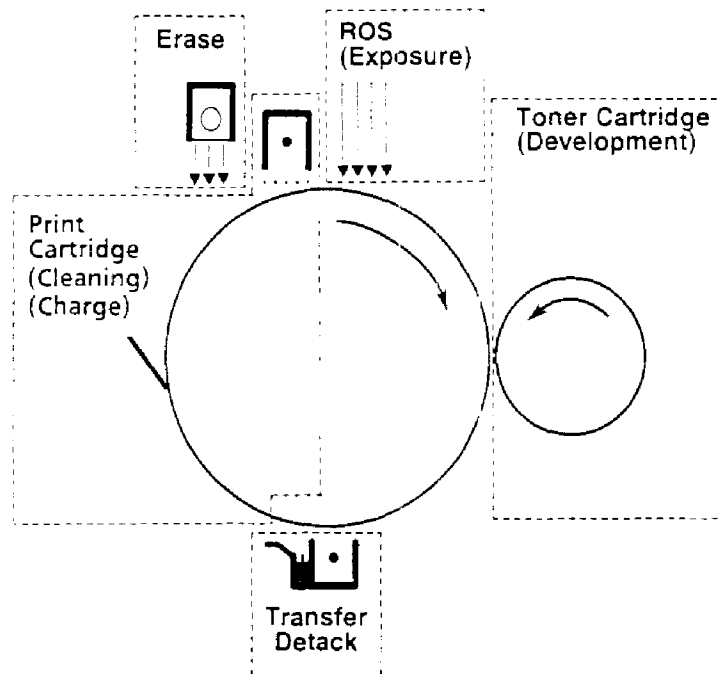


Figure 1: The xerographic proces.

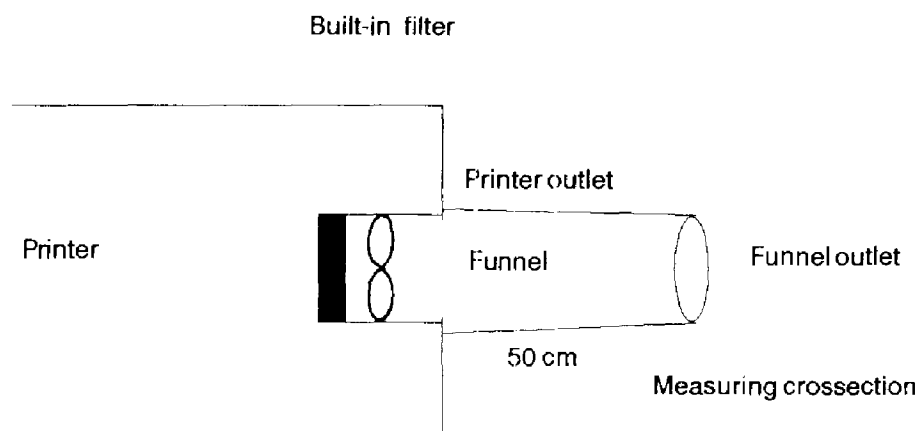


Figure 2: Test principle.

MEASURED EMISSIONS OF OZONE

With and without build-in filters

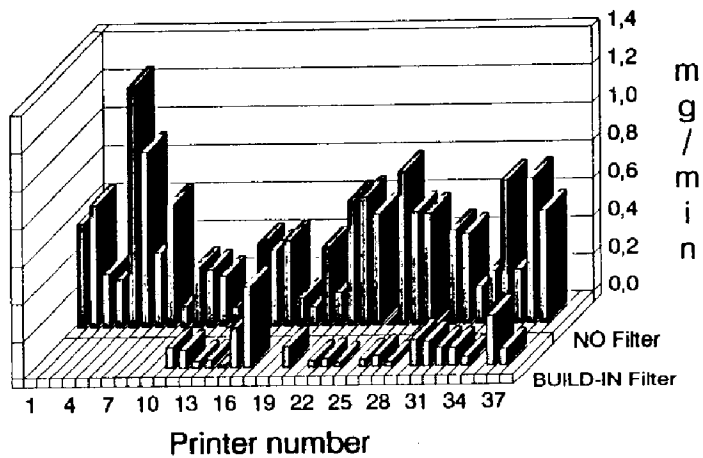


Figure 3: Ozone emissions

PRINTERS WITHOUT FILTER

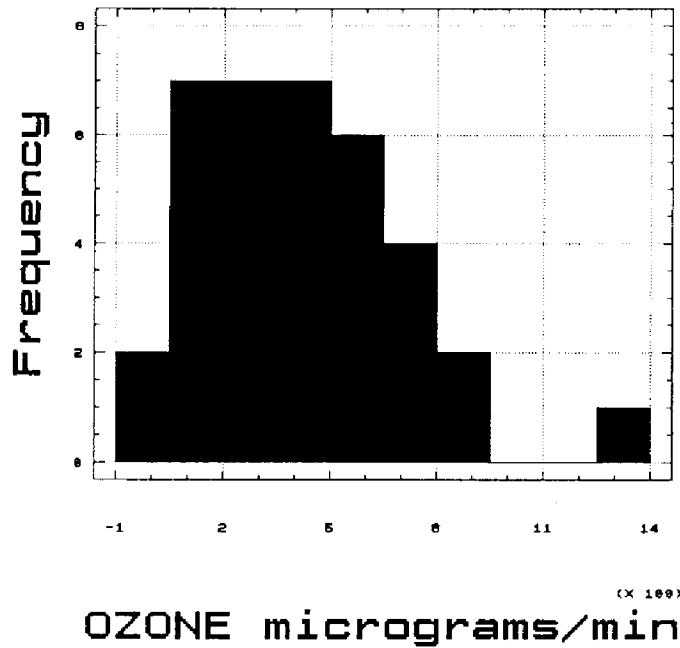
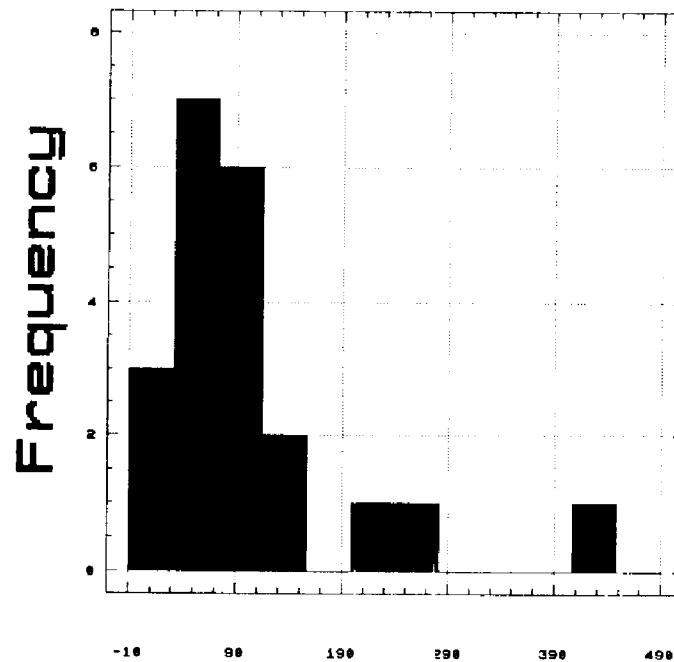


Figure 4: Ozone emissions from printers without built-in filter. Histogram.

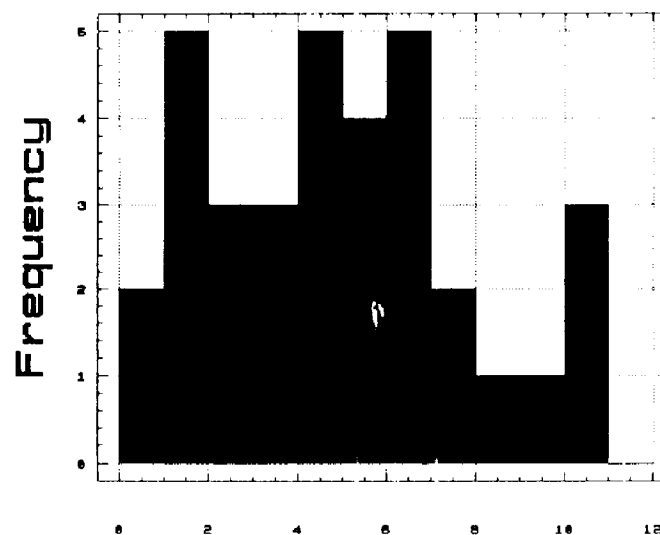
PRINTERS WITH BUILD-IN FILTER



OZONE microgr./min

Figure 5: Ozone emissions from printers with built-in filter. Histogram.

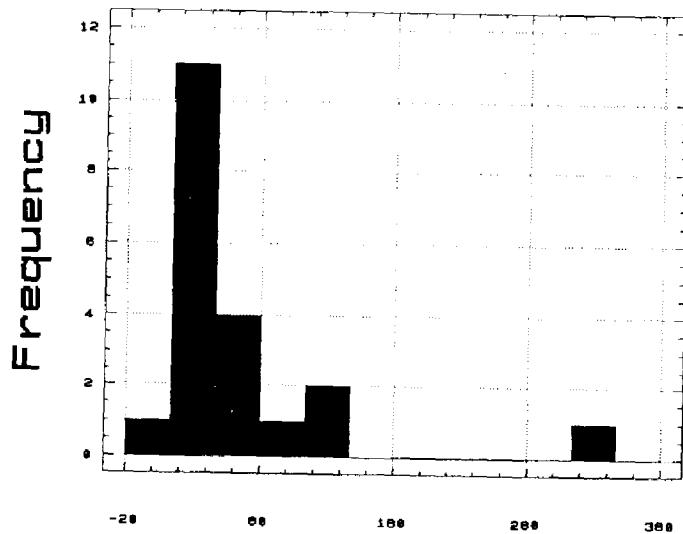
PRINTERS WITHOUT FILTERS OR POOR FILTER



OZONE CONC. microgr./min

Figure 6: Ozone emission concentrations. Histogram.

PARTICULATES FROM PRINTERS



PARTICULATES microgr./min.

Figure 7: Particulate emissions.
Histogram.

OZONE CONTRIBUTIONS FROM PRINTERS

equilibrium concentrations

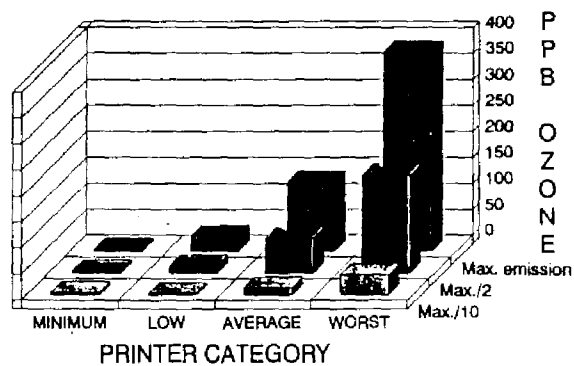


Figure 8: Calculated equilibrium
concentrations.

DETERMINATION OF LIGHT AND HEAVY HYDROCARBONS
AND NON-METHANE ORGANIC COMPOUNDS (NMOC) IN
AMBIENT AIR USING A COMBINATION OF METHOD TO-12
AND METHOD TO-14

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The relationship between ambient concentrations of precursor organic compounds and subsequent downwind concentration of ozone has been described by a variety of photochemical dispersion models. The most important application of such models is to determine the degree of control necessary in an urban area to achieve compliance to air quality standards for ozone. Elaborate theoretical models require detailed organic species data obtained by multi-component gas chromatography. The combination of techniques found in TO12 and TO14 allow for successful identification and speciation of photochemical reactive organic gases (ROG). How the merging of the two methods was applied to the analysis of ROG samples and what commercially available equipment was utilized will be discussed.

INTRODUCTION

The analytical strategy for method TO-14 involves using a high-resolution gas chromatograph (GC) coupled to one or more appropriate GC detectors. Method TO-12 utilized the same type of cryogenic concentration technique used in Method TO-1 and Method TO-14 for high sensitivity with the simple flame ionization detector (FID) of the GC for total MNOC measurements without the GC columns and complex procedure necessary for species separation.

Approaching the analytical system as an in vivo ambient sample is the best way to see how the two methods were merged. Once the canister containing the collected sample is attached to the analytical system, a gas stream flow is established. As in Method TO-14 a Nafion dryer is used to remove water vapor to avoid its formation in the analytical system. Method TO-12 did not utilize the dryer concept. The sample is directed to the cryogenic trap and the ROG's are collected in the cryogenically cooled trap. After a set time the cryogen is then removed and the temperature of the trap is then raised. The ROG's originally collected in the trap are revolatilized and transferred into the gas chromatographic system.

EXPERIMENTAL

As ambient methods have been adopted, modification and adaptations have made use of technical advancements and improvements. Compendium Method TO-1 used cryogenic cooling of the GC inlet to trap the desired analytic. Compendium Method TO-2 used an efficient trap off-line that trapped and transferred compounds into the gas chromatograph. Compendium Method TO-3 made use of the Nafion dryer to reduce moisture, an offline cryogen cooled trap and multidetector analytical system. Analytical methods employing trapping concepts are identified in Table 1.

For the ROG analysis discussed in this TO-12/TO-14 Method a commercially available system is utilized. A Nutech Model 8533 universal sample concentrator is interfaced to the gas chromatograph. The model 8533 sample concentrator consists of two sample concentrator devices, a standard Tenax/charcoal trap for traditional purge-and-trap operations, and a Compendium Method TO-14 liquid cryogen trap. This concentration technique is utilized for many instrumental-analytical methods (i.e., Gas Chromatography: 501, 601, 602, 8020, 8010, 603 and 8030; and Mass Spectrometry: 501.3, 524, 624, 8240, 5040 and 5030.)

When in use for ambient air methods the Model 8533 valve oven is kept at a constant elevated 150 C. The only valve utilized is the cryo-valve to switch the off-line trap in line with the gas chromatograph analytical column. Compendium Method TO-12 collects data valid for the Empirical Kinetic Modeling Approach (EKMA) which does not require speciation.

Since speciation is important for many projects, the non-methane organic compound (NMOC) identification and separation is accomplished by transferring a "discrete bullet" of collected NMOC onto a fused silica high resolution capillary column. The column, which is cryogenically cooled and slowly ramped to a higher separation temperature, allows for optimum separation.

Compendium Method TO-12 takes the cryo-focused sampled directly to a flame ionization detector (FID). The organic compounds previously collected in the trap revolatise due to the increased temperature and they are carried into the FID, resulting a response peak or peaks from the FID. The area of the peak or peaks is integrated, and the integrated value is translated to concentration units by using a previously obtained calibration curve relating integrated peak areas with known concentrations of propane.

In developing this method for NMOC speciation, a Hewlett Packard 5890 Series II Gas Chromatograph was utilized along with a Carle Gas Chromatograph for determining methane and carbon monoxide concentrations. The HP 5890 is considered to have the most stable and reliable heating and cooling control which is quite important for speciation and fingerprinting. Dual detectors are in-place for the same reasons as stated in Compendium Method TO-14. Identification errors can be reduced by: (a) employing simultaneous detection by different detectors, and (b) verification of key components to detect shifts in eluting order or retention time. Interferences on the non-specific detectors can still cause errors in identifying a complex sample. The non-specific detector system (i.e., GC-PID-FID, however, is successfully used for quantification of relatively clean samples. The non-specific detector system can provide a "snapshot" or "fingerprint" of the constituents in the sample, allowing determination of: (1) extent of misidentification due to overlapping or coeluting peaks; (2) position of the ROG within or not within the concentration range desired; and (3) retention time shift patterns.

The O.I. Analytical PID/FID system was chosen for its design and reliability characteristics that made dual detector analysis successful. Sensitivity and linearity are well established with this system.

Compendium Method TO-12 uses electronic integrators for sample quantification. For the ROG procedure a Waters Maxima 820 personal computer based data collection system is utilized to identify and quantify organic analytes. The diagram shown below denotes how the detector sends an analog signal to the chromatographic interface (WD24 board). The magnitude of this signal (measured in microvolts) corresponds to the amount of sample present in the detector at a given time. The chromatographic interface converts the analog signal to digital information.

CONCLUSION

Compendium method TO-12 uses a NIST traceable standard, propane, at the level of 1-100 ppm (3-300 ppmC) for its calibration standard. The importance of the Standard Reference Material (SRM) or a NIST U.S. EPA approved Certified Reference Material (CRM) cannot be overemphasized. This modification or merging of Compendium Methods TO-12 and TO-14 lead to the selection of multiple standards for the ROG procedure. Since speciation is the goal of the ROG analytical scheme, a Hydrocarbon Library of over 200 compounds containing either neat liquids or gas mixtures was established from commercial vendors. The combination of SRM reference standards and these individual compounds yields accurate and adequate identification and quantification. Merging the TO-12/TO-14 Method allows for successful analysis for reactive organic gases and hydrocarbon speciation.

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Table 1
ANALYTICAL METHODS UTILIZING TRAPPING CONCEPTS

Compendium Method	Description	Target Compounds	Pretreatment of Sample	Detector
TO-1	Tenax GC adsorption and GC/MS analysis	Volatile, nonpolar organic (i.e., aromatic hydrocarbons, chlorinated hydrocarbons) having boiling points in the range of 80° to 200°C.	None	GC/MS
TO-2	Carbon Molecular Sieve adsorption and GC/MS analysis	Highly volatile, nonpolar organics (i.e., vinyl chloride, vinylidene chloride, benzene, toluene) having boiling points in the range of -15° to +120°C.	None	GC/MS
TO-3	Cryogenic trapping and GC/FID or GC/ECD analysis	Volatile nonpolar organics having boiling points in the range of -10° to 200°C.	Nafion® dryer to remove moisture	GC/FID GC/ECD
TO-12	Canister collection, cryogenic trapping and GC/FID analysis	Organic compounds specifically hydrocarbons of aromatic, aliphatic and olefinic nature treated as total NMOC.	None	GC/FID
TO-14	Canister collection, cryogenic trapping and GC/MS or GC/FID-PID-ECD analysis	Organic compounds; a detailed list of halogenated and aromatic compounds have been verified down to the ppbV level.	Nafion® dryer to remove moisture	GC/MS GC/FID- ECD-PID
TO-12/14	Canister collection, cryogenic trapping and GC/PID-FID analysis	Organic compounds and reactive gases; methane, carbon monoxide, ethane ethylene, acetylene and a detailed list of parafins olefins, aromatics and terpenes.	Nafion® dryer to remove moisture	GC/PID- FID

SUPERCRITICAL FLUID EXTRACTION - APPLICATIONS IN THE AG INDUSTRY

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In the agricultural industry, the identification and quantification of residual herbicides and their metabolites is crucial to the registration process. Conventional chemical extraction procedures for the parent compound and its metabolites, sometimes unknown, are often difficult, time consuming and risk interference or transformation of the species of interest. Once identified, quantitative recoveries of the residues from the parent compound and its metabolites

The Prediction of Atmospheric Stability and the Dispersion of Emissions from Superfund Sites

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At Superfund sites, remediation procedures may be needed that result in emissions of dense vapors, cooling tower emissions, fumes from elevated vents, and other types of emissions. Because the risk from the remediation activities can occur during specific atmospheric conditions, it is especially important to have access to dispersion models that are both site-specific and weather-specific in order to evaluate the potential effect of (1) remediation activities before they are carried out or (2) accidents after they occur.

This paper discusses of one approach to model mathematically the meteorological conditions that are present in the planetary boundary layer and then to use these calculated conditions to predict the dispersion characteristics of the atmosphere. These theoretical methods can be used for improving the prediction of the dispersion of emissions, especially when the meteorological conditions change during the dispersion, or if there are density effects.

The numerical model dispersion predictions for stable and unstable conditions are similar to the ISC Gaussian dispersion model using the Pasquill-Gifford stability classification system. The numerical model requires a surface heat flux and a geostrophic velocity (wind velocity at an elevated height, 3 km) as input parameters. The numerical model can predict more stable dispersion than the most stable class or more unstable dispersion than the most unstable class, depending on the parameters used.

Basic turbulent dispersion phenomena are discussed and examples are provided for using the computer model for calculating three-dimensional emission concentrations near the site boundary or near a specific source. Dispersion under stable conditions is predicted to be influenced by wind rotation near the top of the planetary boundary layer. Both static dispersion and dynamic dispersion (the wind characteristics change with time) are discussed.

The dispersion of air emissions in our environment is complicated by the wide diversity of source types and the complex nature of air turbulence that disperses these air emissions downwind. Measurements of air concentrations can vary significantly according to the wind speed, the vertical wind shear, the wind direction, and other factors. The dispersion characteristics of vapors in the planetary boundary layer are important because the ultimate fate and environmental impact of vapor releases depend on the path of the vapors and reaction conditions in the wind (such as temperatures and concentrations of trace pollutants). Reaction mechanisms are different at upper elevations in the atmosphere due to differences in radiation and atmospheric conditions.

Conventional approaches to modeling the structure of the atmosphere rely on turbulence parameters and correlations. The applicability of the correlations are limited, so the overall solution must be obtained by integrating a series of different correlations into a unified approach. Danard (1989) presents a good example of this approach.¹

The dispersion of air emissions at specific sites is also important because of potential health risk to workers and the surrounding populations. The theoretical approach presented in this paper provides a method for calculating the wind conditions and for accounting for the effects of vapor density of the dispersed vapors.

The proposed method of calculating the stability characteristics of the atmosphere is based upon a direct calculation using geostrophic meteorological conditions. This numerical method is currently under development, and shows promise because of the power and flexibility of the method.

TURBULENCE

Turbulence is the flow of air in swirls or eddies. The flow of vapors, mists, and smoke follows the flow of the air in the eddies. The flow of air in eddies can be observed in the motion of visible particles in the eddies. At the edge of the eddy swirls, the smoke density is lowered as the eddies mix with surrounding air. This reduction in density is eddy dispersion and it accounts for almost all dispersion of air emissions due to wind.

The region of the atmosphere where the effects of turbulence are most apparent is called the planetary boundary layer (100 m to 3000 m over the Earth's surface). Turbulence can also be important above the planetary boundary layer if there are temperature or density effects. The model of the wind described in this paper uses the same equations for the wind above the planetary boundary layer as are used for the wind below the planetary boundary layer.

The effect of atmospheric structure on dispersion

The atmosphere generally is being heated or cooled by contact with the surface of the planet. Neutral stability occurs near the surface when the surface is the same temperature as the wind over the surface. A situation similar to neutral stability may occur during certain times during the day, with high wind velocities near the surface, or when a heavy cloud cover isolates the surface from solar heating. Turbulent forces shift eddies with a motion that adds a highly variable velocity component to the average wind velocity. At high elevations, the shifting forces due to

turbulent surface interaction are reduced. When the forces due to a density increase in the atmosphere are greater than the forces due to turbulence, the potential for vertical eddy translations is reduced and the atmosphere is more stable. This stability is different at each point in the atmosphere.

Conventional Gaussian dispersion processes assume only one atmospheric stability factor, but the numerical method can be used to continuously update the calculated stability of the atmosphere as a function of both position and time. The ability to change the dispersion characteristics with time permits the calculation of long term dispersion effects.

The flow of air over thermally neutral surfaces is well characterized, even if not well understood. From momentum transport, heat transport, and mass transport correlations developed for flow of fluids in closed conduits, we can predict the turbulent characteristics of air away from surfaces.² The numerical model is based upon the concept of wind flow in discrete eddies, with a shift of position of the eddies from one position to a higher or lower position. The frequencies of these eddy shifts depend on shear forces. The density differences in eddies also contribute to forces acting on the eddy shifts. The density forces are added to the shear forces. If the eddies in the upper layers are more dense, the total forces will be greater than in the neutral case and the eddy shift frequencies will be higher than in the neutral case (this causes unstable conditions). If the eddies in the upper layers are less dense, the total forces will be less than in the neutral case and the eddy shift frequencies will be less than in the neutral case (this causes stable conditions).

The conventional method of estimating the dispersion of vapors from stacks and other sources depends on empirical correlations such as those used with the Industrial Source Complex (ISC) models for air dispersion.³ There are short-term and long-term ISC models which differ in how the results of the dispersion equations are integrated. These models are generally considered as a standard method of predicting the dispersion of vapors from sources. The proposed method of calculating the dispersion characteristics using wind simulation provides a convenient method of accounting for many factors that these empirical methods do not consider, such as the effects of height, changes in conditions, changes in wind direction with time, and plume density.

Model parameters needed for atmospheric simulations

The computer model is designed to simulate the planetary boundary layer from the global perspective. The meteorological parameters needed are those that can be measured or predicted remotely from the location of interest. The only site-specific information that is needed are the surface characteristics. These surface characteristics are expected to be constant, with perhaps seasonal variations in some cases.

The geostrophic wind speed and direction at some distant elevation over the site of interest is an input. Variation of the geostrophic wind with time during the simulation is permitted.

The heat flux from the surface as a function of time is a significant input. The heat flux can be calculated from the solar flux and the surface characteristics, or it can be measured on a site specific basis by interpreting temperature gradients and velocity gradients at the surface.

The temperatures of the atmosphere as a function of height are needed for

the simulation. The model can be used to estimate the temperature distributions from prior meteorological data if limited information about the temperatures is available.

Conventional information about the source that is emitting vapors is needed: area, height, and emission rate.

NUMERICAL MODEL CALCULATIONS

The numerical simulation proceeds with the following simplified flow structure:

- The vertical temperature profile is calculated from the available input data. Linear interpolation between data points is used and the resulting profile is numerically smoothed.
- The wind velocity vectors in both the x and y horizontal directions are calculated as a function of the vertical position.
- The eddy diffusivities are calculated as a function of the vertical position. The eddy diffusivities (K value) determine the rate of pollutant dispersion in the wind.
- The surface heat flux is calculated from linear interpolation of specified flux data.
- The vertical temperature profile is recalculated by solving Fourier's law. The eddy diffusivities are used to calculate the thermal conductivities of the wind. The resulting equation that describes the changes in temperature with time, is a non-linear second order partial differential equation that is solved by means of Thomas's algorithm.
- The dispersion of an emitted component is carried out with a three-dimensional simulation in a zone defined independently of the wind simulation. Concentrations, the location of the center of the plume, and the horizontal and vertical standard deviations of concentration about the center of the plume are calculated.
- The above steps are repeated with the updated temperature distributions.

A comparison of the model results to conventional dispersion correlations.

When the model results are compared to conventional Gaussian dispersion correlations, it is important to note that the model results depend on wind velocities, surface heat flux, and the prior history of the wind. The model results are continuous and do not follow discrete classes. For the purpose of a comparison between the model results and Gaussian correlations, the standard deviations of the dispersion distributions were obtained by a numerical integration of the results of simulation elements in horizontal and vertical lines intercepting at the point of the maximum plume concentration.

Table 1 compares of one set of unstable atmospheric dispersion predictions of the model to conventional Gaussian predictions (stability class A, the most unstable class). The numerical simulation generated the model of an unstable atmosphere by heating a neutral boundary layer for 2 h at a typical mid-afternoon rate of heating ($0.005 \text{ cal/cm}^2\text{-s}$). The dispersion from a height of 2 m was used for comparison. The horizontal and vertical

dispersion are characterized by σ_y and σ_z , respectively. The simulation results are comparable to the results obtained with Gaussian methods, although the simulation results are non-Gaussian (not normally distributed).

Table 2 compares of one set of stable atmospheric dispersion predictions of the numerical model to conventional Gaussian predictions (stability class F, the most stable class). The numerical simulation generated the model of the stable atmosphere by passing a neutral atmosphere over a cooling surface (-0.000075 cal/cm²-s) for a few hours. The model predictions of the horizontal dispersion were substantially greater than those of the vertical dispersion, due mainly to the wind turning effect (Coriolis effect). The standard deviation of the vertical dispersion predicted by the numerical model at 400 m was less than the Gaussian correlation.

Figure 1 presents a computer simulation of a cross-section of the plume under stable atmospheric conditions 42 m downwind of the source. The three different zones in the figure represent concentrations within a factor of 10, of 100, and of 1000 of the plume maximum concentration. The distortion of the plume is due to predicted wind directional differences at different heights. Figure 2 presents the same simulation as Figure 1, but with 10 g/s release of butadiene, which is heavier than air. The density of the butadiene caused the simulation to predict increased fumigation.

Differences may exist between the dispersion predictions of the two models due to factors not considered in the current version of the numerical simulation, such as terrain effects and wind fluctuations. Experimental data are needed to confirm the use of the numerical simulation, especially where the numerical simulation and the Gaussian predictions are different. Since the Gaussian methods are based on empirical data, the Gaussian methods are considered more reliable for situations that are very similar to the dispersion test conditions. For conditions that differ from the basis of the Gaussian correlations, there may be some advantages with the numerical simulation. The numerical method is not limited by some of the constraints of the Gaussian method.

Figure 3 illustrates fumigation of a stable plume of pollutants as simulated by the model. The height of the release (84 m) is above the planetary boundary layer, but as the sun heats the earth's surface, this boundary layer increases in width until the top reaches the plume's height. When the planetary boundary layer reaches the plume, the plume is rapidly dispersed and the pollutant quickly reaches the earth's surface. This numerical prediction illustrates a capability that is beyond the capability of conventional Gaussian predictions. Both the stable dispersion factors and the unstable dispersion factors of the Gaussian correlations would predict lower surface concentrations after fumigation than are predicted by the numerical method.

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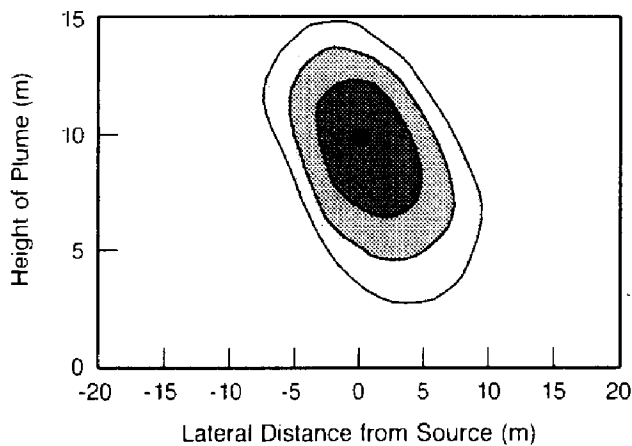


Figure 1. The dispersion of a neutral density plume 40 meters downwind of a point source.

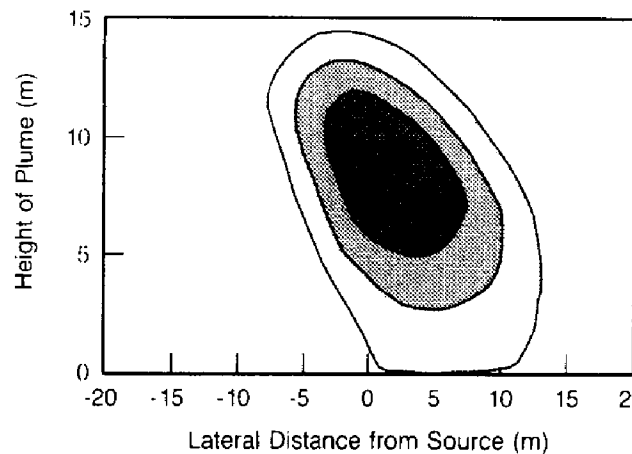


Figure 2. The dispersion of a dense plume 40 meters downwind of a point source.

**Table 1.
A Comparison of Unstable Atmosphere Model Predictions to Gaussian Predictions^a**

Distance from source (m)	Model prediction ^b		Gaussian prediction ^b	
	σ_z	σ_y	σ_z	σ_y
50	6.8	12	7.2	10.3
100	13	23	13.9	20.6
200	26	43	29	40.7
300	38	62	47	60
400	47	65	71	79

^aPasquill-Gifford Stability class A

^b σ_y is calculated at the maximum width of the plume. This occurs at a height that is greater than the point of maximum concentration. σ_y at the point of maximum concentration is somewhat less than σ_z .

**Table 2.
A Comparison of Stable Atmosphere Model Predictions to Gaussian Predictions^a**

Distance from source (m)	Model prediction		Gaussian prediction	
	σ_z	σ_y	σ_z	σ_y
50	2.0	2.3	1.3	1.7
100	2.7	3.3	2.3	3.3
200	3.4	5.7	3.1	6.8
300	3.7	8.4	4.6	9.9
400	4.2	11.7	7.0	13

^aPasquill-Gifford Stability class F

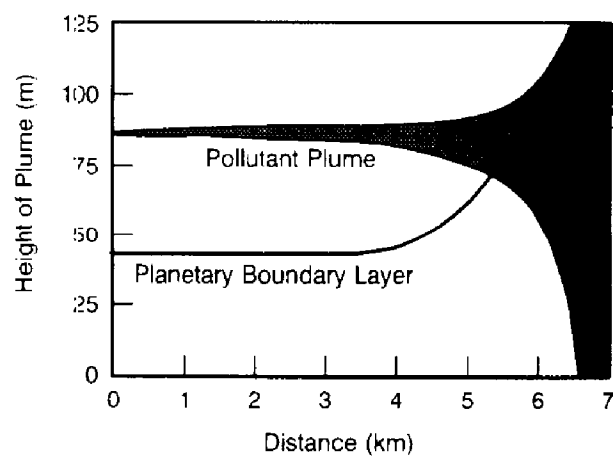


Figure 3. The fumigation of a stable plume as the planetary boundary layer increases with surface heating.

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from the appropriate soil, plant or animal matrix are performed.

We have demonstrated supercritical fluid extraction as a technique that has eliminated some of the tedious steps of current liquid-liquid and solid-liquid extraction procedures. Extraction procedures can be developed in series, or in parallel, to selectively remove several components, either individual compounds, their metabolites or known interferences, from complex matrices.

The extraction of several components of interest, has been conducted on a quantitative basis for common agricultural compounds.

Introduction

SFE has shown great potential in offering shorter extraction times with higher recoveries(1-6). Sample handling is minimized and loss due to several time consuming extraction steps is eliminated. Cleaner sample extracts and more accurate results can be obtained.

The SFE studies presented focus on optimizing recoveries for methylphenylureas and sulfonylureas, agricultural compounds applied to a variety of crops. The environmental fate of these compounds and their metabolites in a variety of soil matrices is determined for identification and quantification purposes. Carbon-14 radiolabeled species of interest were extracted from both Day 0 and aged soils. The resulting radiolabeled extraction effluent was collected, counted via liquid scintillation counting, and overall efficiencies were quantitatively evaluated.

Extraction conditions have been explored in terms of mobile phase modifier, extraction phase additives, pressure or

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density, temperature, equilibration time and extraction mode i.e. either static or dynamic.

In order to examine the extraction effluents, SFE has been coupled to SFC and LC. However, more rapid method development is obtained with off-line examination of the extraction effluents. Typical residue studies require detection limits in the parts per billion range. Large injection volumes along with column switching techniques have been used to obtain the desired detection limits.

Experimental

1. Sample Preparation: Samples are prepared for extraction by filling a hollow stainless steel tube (5 cm x 4.6 mm) with the matrix to be extracted. Alternatively, a cartridge holder for a liquid chromatography guard column can be used. Little sample pretreatment is required. Soil samples are generally sieved and the larger pieces of debris and stones removed. Plant materials are chopped or ground to obtain smaller particle sizes, often the matrix has been freeze-dried before this treatment. Stainless steel frits, 0.045 μm , are used at both ends of the extraction vessel to prevent the loss of the matrix during the extraction. Known amounts of reagent grade sand were also packed at both ends to prevent clogging of the frits by fine particles in the matrix.

Day 0 samples were prepared in the laboratory. Known amounts of the species of interest were spiked onto the matrix of interest from solutions dissolved in methylene chloride. The excess methylene chloride was evaporated under a nitrogen stream. Aged samples were from actual field studies of the compounds of interest. These samples were subjected to the natural aging processes due to weather and compound degradation for the time periods described.

2. Instrumentation: The extraction experiments were conducted on three instruments with equivalent results obtained although not over equivalent time periods. These instruments were: a Hewlett Packard 1082 liquid chromatograph that had been modified for supercritical fluid delivery (4), a Lee Scientific Model 501 supercritical fluid chromatograph that was modified with a Rheodyne No 5704 tandem switching valve, and a Suprex Model 200A dual oven SFE/SFC.

The liquid chromatographic experiments were conducted using a Hewlett Packard 1090 LC. The liquid chromatograph was equipped with a photodiode array detector and a column switching valve to expedite sample clean-up.

3. Extraction mode: Static and dynamic extraction conditions were used in these experiments. In static extraction, the mobile phase was allowed to remain in contact with the sample matrix for a predetermined time period. In the dynamic mode, the extraction fluid was pumped continuously through the extraction vessel.

Results

Table 1 shows the results of experimentation comparing classical methodology with SFE under a variety of conditions. The addition of extraction phase modifiers demonstrated the need for these additives to obtain the desired high recoveries. Without them, acceptable recoveries were not obtained. The volume of the extraction phase additive was found to be optimum for a given sample size, but excess additive did not reduce acceptable recoveries. In certain cases, an optimum modifier has been found, but in general methanol seems to be the most universal modifier to achieve high extraction efficiencies.

Static extraction was found to enhance recoveries during shorter time periods. This is especially useful when the extraction is coupled with on-line chromatography or analysis. In this way, larger amounts of solute of interest can be transferred in a shorter time period.

Table 1

Compound	Time	Modifier Volume	Method	Recovery
Diuron	35 min	0.0 mL	static-dynamic SFE (CO ₂ mobile phase)	0%
Diuron	35 min	200 µL methanol	static-dynamic SFE (CO ₂ mobile phase)	99%
Diuron	50 min	200 µL methanol	dynamic SFE (CO ₂ mobile phase)	86%
Diuron	105 min	50.0 mL methanol	dynamic SFE (CO ₂ modified mobile phase)	99%
Diuron	3 days	> 1 Liter of mixed solvents	Classical extraction methodology with separatory funnels	96%
Diuron	35 min	0.0 mL	dynamic SFE (CO ₂ mobile phase)	0%

Increases in temperature were found to enhance the extraction efficiencies of Diuron and Linuron, phenylmethylurea compounds. The volatility of these compounds (boiling points less than 100°C) could account for this effect. In actuality, the reverse trend would be expected

since lower temperatures would yield higher densities thus enhancing the recovery. In the cases examined, the phenylmethylureas, sulfonylureas, and their metabolites, increases in density or pressure have increased the extraction efficiencies obtained.

Conclusions

Reproducible, quantitative recoveries have been obtained for the extraction of these moderately polar compounds from soil matrices. Optimization of the experimental method is rapid. Overall SFE offers the versatility that is needed to become a dependable analytical sample preparation technique.

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ISOLATION OF POLYCHLORINATED DIBENZO-P-DIOXINS AND DIBENZOFURANS FROM FLY ASH SAMPLES USING SUPERCRITICAL FLUID EXTRACTION

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The use of supercritical fluid extraction yields rapid and quantitative extraction of polychlorinated dibenzo-p-dioxins and dibenzofurans from municipal incinerator flyash. One hour of extraction with nitrous oxide (N_2O) at 400 atm and 40°C removes over 90% of the tetrachlorodibenzo-p-dioxins from flyash compared to 20 h of extraction with the Soxhlet method. Pure carbon dioxide (CO_2), which does not remove dioxins at 400 atm, can be used in a clean-up procedure to remove weakly adsorbed organics. However, CO_2 at 400 atm and extraction temperature of 60°C does isolate dioxins when 10% benzene is used as a modifier, or when the flyash matrix is etched with hydrochloric acid. The extraction rate is controlled by the kinetics of desorption and not by solubilities. The presence of carbon in flyash inhibits the isolation of dioxins. Also, particle size and or porosity of the material significantly effects the extraction process.

Preliminary results indicate that some sorbents may be used, in combination with supercritical fluids, in the clean-up procedure of complex matrices such as flyash. This process is similar to that used in solid phase extraction. In this procedure, however, the supercritical fluid replaces the organic solvents. Polychlorinated biphenyls were partially fractionated from polychlorinated dibenzo-p-dioxins using TENAX-GC. Similar results were obtained with graphite at 650 atm and 40°C using benzene modified N_2O .

Introduction

The public's concern with the presence of a number of toxic chemicals in food and environmental samples has created a demand for improved methods of analysis of these compounds. The problem associated with municipal refuse disposal increases as the population of North America increases. Incinerators are now used to eliminate the problems associated with dumping the waste in landfill sites. Thousands of tons of municipal incinerator flyash are produced annually with 1-2% escaping into the atmosphere through stack emission. However this industry has come under criticism with the discovery of polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) in municipal incinerator fly ash.

The first step in environmental analysis of solids such as municipal incinerator fly ash involves separating the organic compounds of interest from the matrix. This process is presently achieved by using liquid extractions. This method is time consuming and very expensive since it requires high purity organic solvents. It also generates a significant amount of toxic waste since the solvent recycling process is very difficult to implement.

However, after extraction a complex organic mixture remains which, often requires application of clean-up procedures to remove interferences for proper quantitation of trace compounds. At the present time the only methods used require large amounts of organic solvents, are labour intensive and difficult to automate. For example, current clean-up procedures for the determination of PCDDs/PCDFs present in complex samples involve several chromatographic column separations and require days to complete.

An attractive alternative is supercritical fluid extraction (SFE). This approach has been explored for some time by chemical engineers¹⁻³ and has recently attracted the attention of analytical chemists⁴⁻¹⁰. Supercritical fluid extraction exploits the properties of this medium at temperatures and pressures near the critical point. This method combines both distillation and extraction in a single process since both vapour pressure and phase separation are involved. The major features of supercritical fluid extraction include: low toxicity of the supercritical carbon dioxide with its low cost and high chemical inertia; low temperature extractions of non-volatile compounds; selectivity of the process through density programming (by varying the fluid pressure); rapid extractions due to low viscosity of fluids and high diffusivities compared to liquids; easy separation of the solute from the mixture by lowering the pressure; and low energy consumption due to low temperatures of adsorption and desorption compared to the high thermal energy required for distillation. Organic solvents can be replaced by supercritical fluids and sorbents in the clean-up procedures of complex organic mixtures (such as flyash) produced after SFE of complex environmental samples.

Experimental

Distilled in Glass Grade solvents (benzene, methanol, hexane, and dichloromethane) used in this study were purchased from BDH Chemicals, Toronto,

Ontario. The liquified, bone-dry carbon dioxide, nitrous oxide, helium, and nitrogen were acquired from Inter City Welding, Kitchener, Ontario. The flyash was supplied by the Ontario Ministry of Environment from an electrostatic precipitator of a municipal incinerator in Toronto, Ontario.

In order to obtain reproducible results, the flyash to be extracted was sieved to 150 μm . Approximately 10 g samples were Soxhlet extracted with benzene (300 mL) for 40, 20, 6 and 2 h. Coarse porosity glass fritted extraction thimbles were used in the extractions. The solutions were reduced in volume by rotary evaporation, transferred to a 25 mL pear flask for further concentration and then concentrated, in a vial, to 500 μL by a gentle stream of nitrogen.

A high pressure vessel¹¹ was used to supply supercritical fluids for extractions. The extraction vessel, with a capacity for 0.8 g of flyash, was constructed of Swagelok 316 stainless steel (SS) fittings and 5 cm x 1/4" SS tubing. A fused silica capillary, 20 cm x 20 μm , was connected to the extraction vessel with a graphite-vespel ferrule. The capillary was directed into a 1.5 mL vial with septum and vent containing approximately 1.0 mL of hexane. A measured flow rate of approximately 120 mL/min of the depressurized gas was obtained at 400 atm. The samples were concentrated to 100 μL by directing a gentle stream of nitrogen into the vial.

The extraction of PCDDs/PCDFs was accomplished in three different ways. Benzene (10% by volume) was added to the CO_2 in the high-pressure vessel. A pressure of 400 atm was used to extract the PCDDs/PCDFs at 60°C for 2 h. Secondly, nitrous oxide (with no modifier) was used as the supercritical fluid. The temperature of the extraction was 40°C for 2 h at an extraction pressure of 400 atm. The flyash was treated with 1 N HCl to break down the matrix and facilitate the ease of the extraction of the PCDDs/PCDFs. The flyash was then stirred for 2 h in 1N HCl, centrifuged, washed with copious amounts of distilled water, and air-dried. CO_2 was used to extract it at 400 atm for 2 h and 40°C. This flyash was also extracted with nitrous oxide at 400 atm for 2 h and 40°C. In the above SFE procedures, approximately 0.5 g of fly ash was extracted.

A Varian 3500 capillary gas chromatograph, equipped with an on-column capillary injector, an electron capture detector (ECD), flame ionization detector (FID) and 30 m x 0.25 μm fused silica capillary column (DB-5)(J & W Scientific, California) was used for chromatographic analysis.

Quantitation of the extracted PCDDs/ PCDFs was achieved with a Hewlett-Packard HP5890 GC-MSD system. An ionization voltage of 70eV and ion source temperature of 300°C were used. Before each set of analyses, the instrument was tuned with the compound perfluorotributylamine (PFTBA). This compound was used since it is stable and produces fragments throughout the entire mass range. Three such peaks at m/z 264.00, 413.95, 501.95 were used since they are close to the ion masses of the PCDDs and PCDFs. Since the mass of the PCDDs and PCDFs are known, selected ion monitoring (SIM) was used. SIM of the $(\text{M}-\text{COCl})^+$, M^+ , and $(\text{M}+2)^+$ ions for the $\text{T}_4\text{CDD}/\text{T}_4\text{CDF}$ through the $\text{H}_7\text{CDD}/\text{H}_7\text{CDF}$ were used for identification. The $(\text{M}-\text{COCl})^+$, $(\text{M}+2)^+$, and $(\text{M}+4)^+$ ions were monitored for the $\text{O}_8\text{CDD}/\text{O}_8\text{CDF}$. M denotes the parent molecule. To ensure correct identification and quantitation of PCDDs and PCDFs, a standard mixture of these compounds was injected before a new set of unknowns was analyzed. A DB-5 column was also used

for GC-MSD analysis. The temperature program consisted of an initial oven temperature of 65°C for 1 min, programmed to 230°C at 15°C/min, held there for 1 min, programmed to 300°C at 3°C/min, and held there for 30 min.

One percent and ten percent (by weight) carbon was added to approximately 10 g of flyash and mixed. Approximately 0.4 g of this mixture was extracted at 400 atm and 40°C for 2 h with N₂O. These samples were concentrated to 100 µL with nitrogen and analyzed with the Varian 3500 GC.

The sorbents (except for TENAX-GC which was cleaned at 400atm for 2 h with N₂O) were extracted with the Soxhlet method for 20 h with 250 mL benzene to remove interfering compounds. Coarse porosity glass fritted extraction thimbles were also used in these extractions. The sorbents were air dried and approximately 0.2 g were used in supercritical extractions. A solution consisting of tetrachlorobenzene (T₄CB), hexachlorobenzene (H₆CB), trichlorobiphenyl (P₃CB), pentachlorobiphenyl (P₅CB), 1,2,3,4-tetrachlorodibenzo-p-dioxin (T₄CDD), octachlorodibenzo-p-dioxin (O₈CDD) was spiked (100 µL) onto the sorbents. The sorbents were extracted at 400 atm and 40°C with CO₂ and N₂O. 100 µL methoxychlor was used as the internal standard. Fractions were collected after 5, 10, 15, 25, 45 and 90 minutes. These samples were concentrated to 100 µL with nitrogen and analyzed with the Varian 3500 GC.

Results and Discussion

The method validation procedure was complicated by the lack of certified standards of flyash. Therefore, in order to evaluate the accuracy, the SFE method was directly compared with the standard Soxhlet extraction procedure. Analyses were reproduced at least seven time to ensure good estimation of the accuracy and precision of the analytical results. Also, different batches of material were analyzed to ensure good efficiencies of SFE for a range of contamination levels¹².

Initial results obtained with SFE were very discouraging. No native pollutants were removed from flyash using pure CO₂ at 6000 psi. However, ¹³C labelled standard spikes of 2,3,7,8-tetrachlorodibenzo-p-dioxin was successfully recovered from the flyash matrix. This result clearly indicates that native dioxins and furans are strongly bound to the matrix; they are most likely chemisorbed onto the original active sites where they were formed (Figure 1). In this situation the extraction process is kinetically limited. The large energy barrier associated with dissociation of the analyte-matrix complex prevents the effective extraction. This is in contrast to the case when analyte molecules are physically adsorbed onto the matrix when the equilibrium described by the corresponding partition coefficient K is reached rapidly limited only by the diffusion coefficients. In order to facilitate extraction with CO₂ at 400 atm it was decided to etch the matrix with hydrochloric acid in order to eliminate chemisorption sites and the desorption energy barrier associated with it. This resulted in complete removal of native pollutants (Table I), but this procedure required an additional step. The precision of data was also poor due to highly inhomogeneous material produced after treatment of the matrix with acid. Therefore, in the next step small amounts of benzene were added to supercritical carbon dioxide. This solvent

was chosen because it has been proven to be effective in Soxhlet procedures. Indeed, quantitative removal of native dioxins was achieved with this approach. However, this procedure was less desirable as it used toxic solvents and replacement of this solvent with methanol resulted in lower extraction efficiencies. In the final procedure nitrous oxide, a slightly polar gas which has been proven to extract polyaromatic molecules more rapidly, was used at 400 atm. Using this procedure the native dioxins and furans were quantitatively removed from the untreated fly ash matrix. The extraction time is about 1 h versus 20 h for Soxhlet extraction.

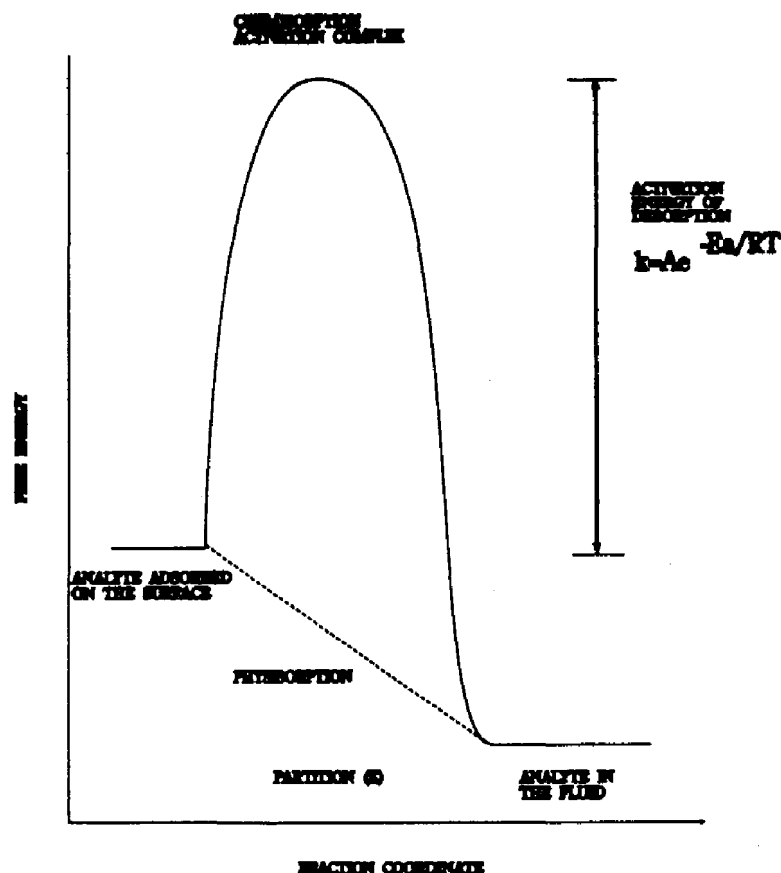


Figure 1 Activation energy barrier

GROUP OF COMPOUNDS	CO ₂ + 10% benzene 400 atm 60°C 2 h	CO ₂ acid treated fly- ash, 400 atm 40°C 2 h	N ₂ O 400 atm 40°C 2 h
POLYCHLORINATED DIBENZODIOXINS TOTAL	92.4±9.8	86.5±11.4	84±4
T ₄ CDD	117±12	96±25	98±7
TOTAL POLYCHLORINATED DIBENZOFURANS	91±13.6	96.4±10.4	88±4

Table I Percent extraction efficiencies, as compared to 20 h Soxhlet method, of polychlorinated dibenzo-p-dioxins and dibenzofurans from flyash with supercritical fluids.

The dramatic difference between SFE results obtained from CO₂ and N₂O, structurally similar molecules, is somewhat unexpected. We believe that investigations prompted by this result will lead to a better understanding of the nature of supercritical fluid extraction. We are presently studying the extraction rates of the native dioxins and furans from flyash as a function of the SFE polarizability/polarity parameter by varying the fluid density. The initial results indicate that the nitrous oxide fluid molecules are involved in a specific interaction with the matrix which lowers the activation energy barrier to the desorption of chemisorbed molecules.

The difference in extraction efficiencies between CO₂ and N₂O can be used effectively to clean-up complex organic mixtures which are present in the flyash. Weakly adsorbed interferences can be removed first with CO₂ followed by extraction of compounds of interest with N₂O. In addition, our more recent results indicate that pure CO₂ is capable of removing native dioxins and furans from fly ash matrix when the extraction pressure is 650 atm or higher.

The results outlined above clearly illustrate the procedures which can be used to optimize conditions for supercritical fluid extraction. It appears that by increasing the pressure, and therefore the density and polarizability of the fluid, the desorption strength of the fluid increases. These observations emphasize the difference between the engineering applications of the supercritical fluid extraction, where relatively large amounts of the product are dissolved in the fluid and transferred to the collection vessel, and the trace analysis applications where minute quantities of specifically adsorbed material must be removed quantitatively from the matrix. In order to achieve the engineering goal, it is, in most cases, sufficient to ensure that the material of interest is soluble in the supercritical fluid, while to ensure quantitative removal of pollutants, it is necessary to use a strong solvent that will remove organic components from the matrix.

Our experience with the flyash matrix indicates that the extraction efficiencies obtained for a spiked standard can be drastically different than those for native pollutants. It is difficult or, in some cases, impossible to prepare spiked standards which are equivalent to native contaminants, due to aging effects associated with phenomena such as chemisorption and porosity effects¹³⁻¹⁴. Therefore, estimation of accuracy of analytical methods by procedural spikes need to be treated with caution. Preliminary results indicate that even different size flyash particles yield significant extraction profiles.

There is some concern that carbon levels in flyash affects the SFE recoveries of PCDDs/PCDFs. This is critical to the general applicability of the SFE method as the type of refuse, the incineration temperature and the fuel used may affect carbon levels in the ash. It is known that carbon adsorbs PCDDs/PCDFs, as the final step in the clean-up procedure of complex samples¹⁵ consists of a carbon column. Initial results involving 1 % and 10 % carbon revealed that carbon does indeed prevent the extraction of PCDDs/PCDFs from flyash. 51.9% of O8CDD was isolated from the flyash matrix when 1 % carbon was added. The extraction of this compound dropped to 18.3% when 10% carbon was added to flyash. Both carbon and PCDDs have a planar structure which allows for a greater adsorption of these compounds by carbon.

Various sorbents are used in model studies for the extraction of environmental

pollutants. A number of these sorbents (TENAX-GC, CN, C₁₈ and graphite) were used to investigate the possible clean-up of organics from environmental matrices. This fractionation scheme resembles the process of solid phase extraction except, the organic solvents are replaced by supercritical fluids.

Ideally, a sorbent will retain all compounds initially, but release progressively less soluble compounds as the pressure is increased. Initial results indicate that C₁₈ and CN produced full recoveries of T₄CB, H₆CB, P₃CB, P₅CB, T₄CDD, O₈CDD after 5 minutes of extraction with both CO₂ and N₂O.

Two possible sorbents that may be used to clean-up complex organic mixtures are graphite and TENAX-GC. Extractions of graphite at 650 atm with N₂O removed T₄CB, H₆CB, P₃CB, and P₅CB. Addition of benzene, as a modifier, recovered the planar T₄CDD. N₂O extraction of Tenax produced quantitative recoveries in 5 minutes. However, CO₂ was able to fractionate some of the compounds. The T₄CB and H₆CB were extracted in the first 5 minutes while P₃CB was isolated in the first 10 minutes. The O₈CDD was removed in the last hour. Therefore, both Tenax and graphite may be used to clean-up complex mixtures produced after SFE of samples such as flyash.

Conclusions

The time necessary to isolate dioxins from municipal incinerator flyash was reduced from 20 h with the Soxhlet method to 2 h with supercritical fluids. Substantially smaller quantities of flyash are needed in SFE than with the Soxhlet method. Furthermore, the limiting step in the extraction rate appears to be the kinetics of desorption rather than the solubilities of these species in CO₂ or N₂O. The variance and standard deviation associated with supercritical fluids was lower than that of the Soxhlet method.

The presence of carbon in flyash reduces the efficiency of the isolation of PCDDs/PCDFs from the matrix.

Some sorbents may be utilized in the same manner as in solid phase extraction for the clean-up of complex organic samples. Clean-up procedures can be based on changing the supercritical fluid, addition of a modifier or varying the pressure.

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EXTRACTION AND SEPARATION OF POLAR MOLECULES USING
SUPERCRITICAL FLUIDS WITH SUBSEQUENT IDENTIFICATION
BY FT-IR SPECTROMETRY

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Organic compounds of medium polarity can be rapidly and efficiently extracted from most solid substrates with neat supercritical carbon dioxide. The difficulty of extracting organics using supercritical fluids increases with the polarity of both the analyte and the substrate. Extraction efficiency can usually be increased under isobaric conditions by increasing the temperature, even though the density of the fluid may be decreased. Extraction efficiency is also increased by the addition of polar modifiers to CO₂. Extracts are condensed on a short length of an appropriate chromatographic column mounted immediately after the restrictor, and separated as soon as the extraction is believed to be complete. A generalized method of trapping chromatography elutes as small spots on a moving ZnSe window has allowed Fourier transform infrared (FT-IR) spectra of low nanogram and subnanogram quantities of organic analytes to be measured in real time. This chromatography/FT-IR interface provides a complementary technique to mass spectrometry through which the substitutional isomers of aromatic compounds can be readily distinguished. The performance of the supercritical fluid extraction/supercritical fluid chromatography/FT-IR spectrometry interface is illustrated by the extraction and identification of polychlorinated biphenyls from soils.

The ease of extracting organic molecules from solid matrices using supercritical carbon dioxide decreases both with the polarity of the molecules being extracted and that of the matrix. The closer is the polarity of any molecule to that of the extractant the greater is its solubility. Since CO_2 is a nonpolar (albeit highly polarizable) molecule, compounds of low and medium polarity have the highest solubility. It is often assumed that the density of supercritical fluids controls their solvent strength. Certainly for extractions carried out isothermally, the efficiency increases with pressure, as not only does the density increase but also the mass flow rate through a given restrictor increases with the pressure differential. For fluids at a constant density, the solubility of organic molecules increases with temperature. Keeping the density constant while varying the temperature often necessitates a disproportionately large variation in pressure. We have found that extraction efficiency often increased with temperature at a given pressure (i.e. with a set flow rate), even though the density of the extracting fluid may drop by more than a factor of two.

The ease of extracting organic molecules from solid substrates also depends on the strength of the interaction between the analytes and the substrate surface. The greater the number of hydrogen-bond donors and acceptors contained by the analyte and the matrix, the poorer will be the extraction efficiency, since CO_2 does not interact strongly with hydrophilic substrates or very polar analytes. In this case, the extraction efficiency should be dramatically increased by the addition of a polar modifier such as methanol or water to the CO_2 , as the modifier molecules can form hydrogen-bonded complexes with polar analytes and will interact strongly with OH groups on the surface of the substrate, effectively blocking each active site from interacting with polar analytes.

Polychlorinated biphenyls (PCBs) are analytes of medium polarity that do not interact strongly with siliceous surfaces. It is relatively easy, therefore, to extract PCBs from soils using supercritical CO_2 . The very sharp change in extraction efficiency occurring around 1200 psi is very surprising in light of the relatively slow change in density with pressure. Extraction efficiency was measured by accumulating the extracted PCBs on a short length of a capillary supercritical fluid chromatography (SFC) column for a time of 20 minutes, after which time they were separated by capillary SFC, see Figure 1A. This technique incorporates many of the principles that were developed by Miller and Hawthorne for their supercritical fluid extraction (SFE)/gas chromatography (GC) interface [1]. The total quantity of the extract was estimated by measuring the integrated area under the chromatogram and comparing the result with the integrated area under the chromatogram obtained after a conventional injection of a solution of the same PCB at a known concentration, see Figure 1B. It is equally feasible to trap supercritical fluid extracts on wider bore tubing for subsequent separation by gas chromatography or on short lengths of packed columns for separation by packed column SFC or high performance liquid chromatography (HPLC).

For extractions of standard samples of PCBs in soil (Environmental Resource Associates) at 50°C , the extraction efficiency is strongly dependent on the pressure, as shown in Figure 2. Also shown on this plot is the variation of the density

of CO₂ with pressure at 50°C.

The more polar are the organic analytes, the more slowly they are extracted from polar matrices, presumably because of the existence of strong hydrogen bonding between the analytes and the matrix. This effect is illustrated by the SFE of indigeneous organic molecules from paper using neat CO₂. Supercritical fluid chromatograms of four consecutive extractions of a paper sample are shown in Figure 3. The earlier peaks in the chromatogram are significantly reduced in intensity in Figure 3E, indicating that these components are being extracted at fairly high efficiency. Conversely, the later-eluting peaks do not diminish appreciably in intensity from Figure 3A to 3E indicating that they are more tightly bound to the cellulose matrix and possibly even form a saturated solution under the conditions of the extraction.

The higher the polarity of the analytes, the more difficult they are to solvate and to separate by capillary SFC using neat CO₂ as the mobile phase. Polar analytes exhibit greater peak widths and a greater degree of tailing than nonpolar compounds separated using the same chromatographic parameters. In this case, the addition of a polar modifier to the CO₂ mobile phase will alleviate the problem of tailing, although neither the retention time nor the peak width are changed to a great extent, see Figure 4. For such molecules, reverse-phase HPLC appears to be the optimal separation technique.

The identification of large molecules often requires the combination of several spectroscopic techniques. Mass spectrometry (MS) is the technique of choice for identifying GC elutes, but even for GC the additional measurement of the infrared spectrum reduces the ambiguity of the identification [2]. The higher the molecular weight of the analyte, the more ambiguous is its mass spectrum and the greater is the need for additional spectroscopic data. In view of the complementary nature of infrared and mass spectra, infrared spectrometry would appear to be the technique of choice in this regard. However, interfaces between chromatographs of all types and FT-IR spectrometers are commonly perceived to be of much lower sensitivity than the corresponding chromatography/MS system.

In the past few years, we have shown that "direct deposition" GC/FT-IR [3,4] and SFC/FT-IR [5,6] interfaces significantly reduce the minimum injected quantity required for the measurement of an identifiable spectrum. In these interfaces, each elute is deposited on a moving ZnSe window as a spot of very low area (<0.02 mm²), so that even a 1-ng deposit has a thickness that is sufficient to yield an identifiable spectrum in one second using an FT-IR spectrometer equipped with microscope-style optics. To illustrate the power of SFC/FT-IR measurements based on this principle, the spectra of the six peaks indicated in Figure 1 are shown in Figures 5 and 6, along with the identification of five of these components made solely on the basis of their infrared spectra. The sixth peak appears to be a mixture of at least two unresolved components.

The SFC/FT-IR spectra shown in Figures 5 and 6 were measured by first depositing each component on a ZnSe window at ambient temperature held immediately below the restrictor. The spectra were then measured subsequently using a Perkin-Elmer Model 1800 FT-IR spectrometer equipped with a Spectra-Tech (Stamford, CT) IR Plan microscope, with the aperture set at 100 μm. A GC/FT-IR interface based on the principle of direct deposition is now

available commercially (Digilab Division of Bio-Rad, Cambridge, MA). We are presently modifying this interface for on-line SFC/FT-IR and there is every indication that it will yield equivalent spectra to those shown in Figures 5 and 6. We have already tested this interface with water-modified CO₂, and there is no trace of water in the measured spectra, even when the window is cooled to -20°C.

It was noted above that for very polar analytes, reverse-phase (RP) HPLC will probably yield superior separations than SFC because of the greatly increased polarity of the mobile phase. We are developing a direct deposition RP-HPLC/FT-IR interface which is based on the same principles as the GC/FT-IR and SFC/FT-IR interfaces described above. Aqueous solvents can be eliminated by a concentric flow nebulizer. With flow rates of water up to 50 µl/min, the area of deposits can be reduced below 0.02 mm². This has not yet been applied to true HPLC separations, and it is presently being tested using injections of solutions of a single analyte in a "flow injection analysis" ("FIA") mode. A preliminary spectrum, of 60 ng of methyl violet 2B deposited from 100% water at a flow rate of 50 µl/min measured in this manner is shown in Figure 7. The high signal-to-noise ratio of this spectrum indicates that subnanogram detection limits will be achievable for HPLC/FT-IR in the very near future.

Acknowledgments

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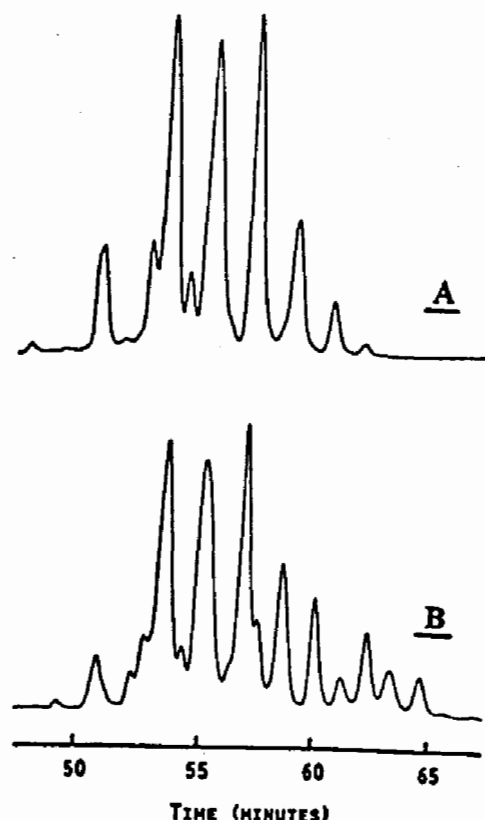


Figure 1. (A) SFC of standard solution of Arochlor 1260 (960 ng injected) after removal of solvent, (B) SFE/SFC of a certified soil sample containing Arochlor 1260. If all the PCBs were removed quantitatively, 910 ng would have been extracted.

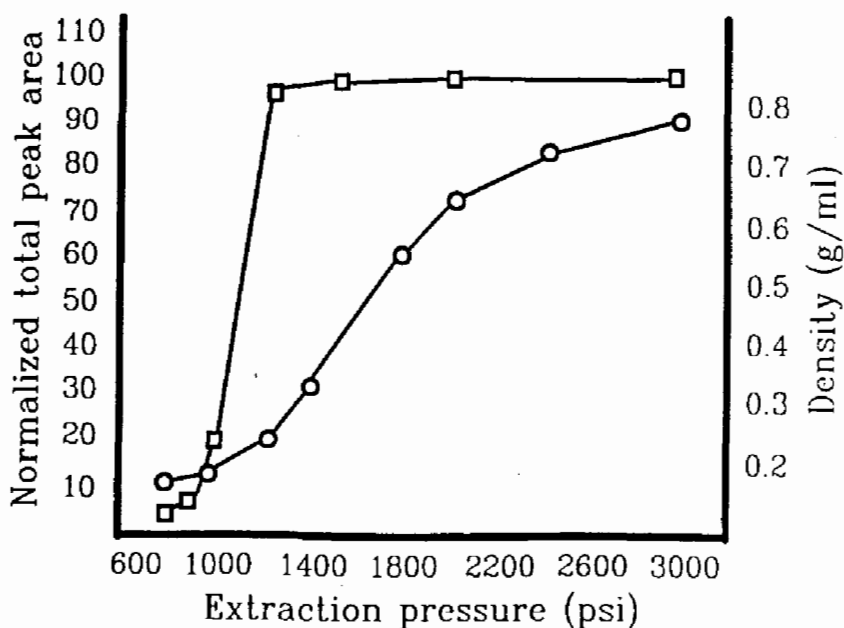


Figure 2. (□) Extraction efficiency as a function of pressure for same certified soil sample used for Figure 1; (○) Variation of density of CO₂ as a function of pressure.

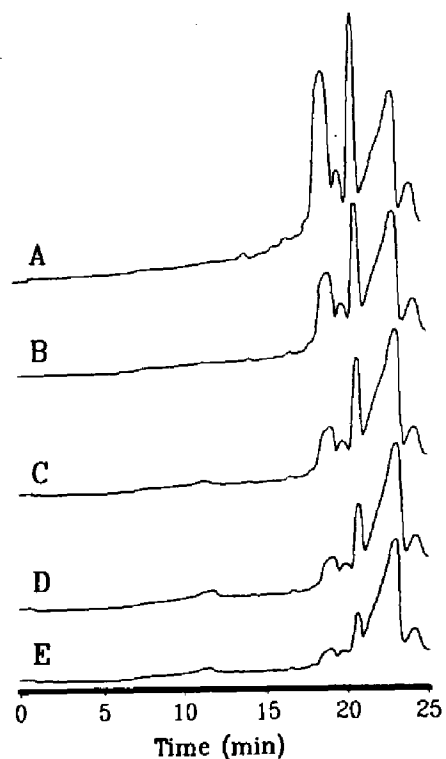


Figure 3. Chromatograms of successive supercritical fluid extractions of a paper sample.

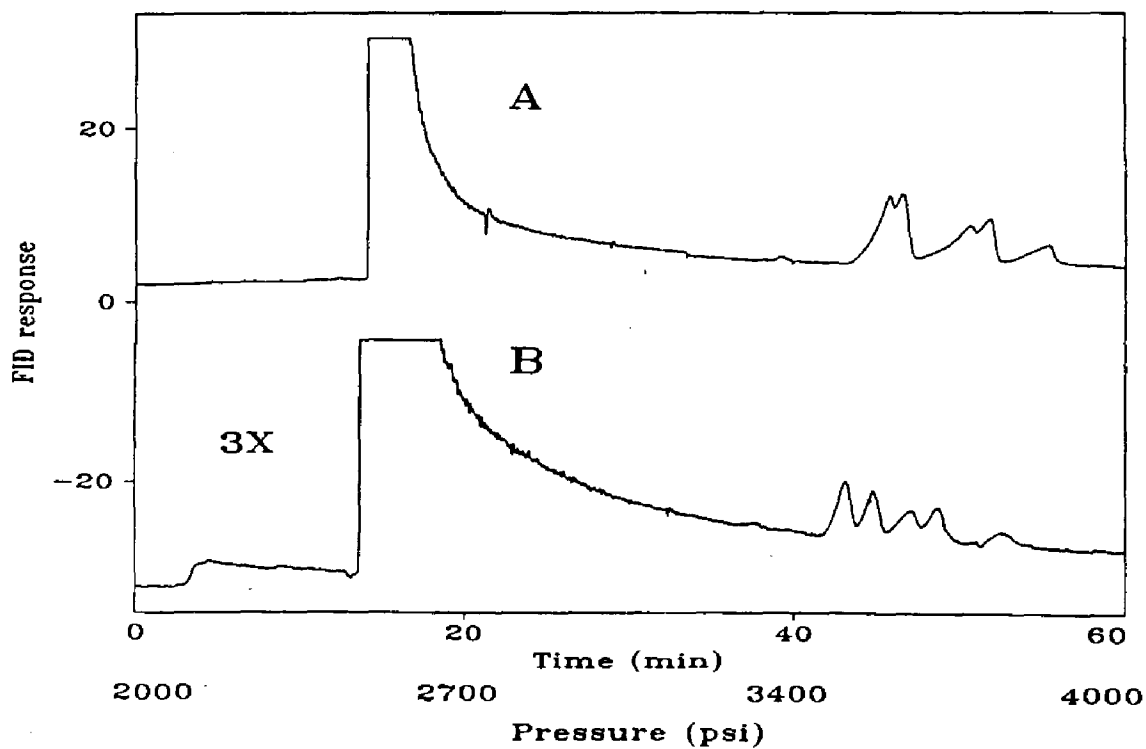


Figure 4. Chromatogram of a mixture of cholic acid derivatives (lithocholic acid, methyl cholate, chenodeoxycholic acid, deoxycholic acid, and cholic acid) separated on a biphenyl capillary column using (A) carbon dioxide, and (B) CO_2 containing 0.1% water.

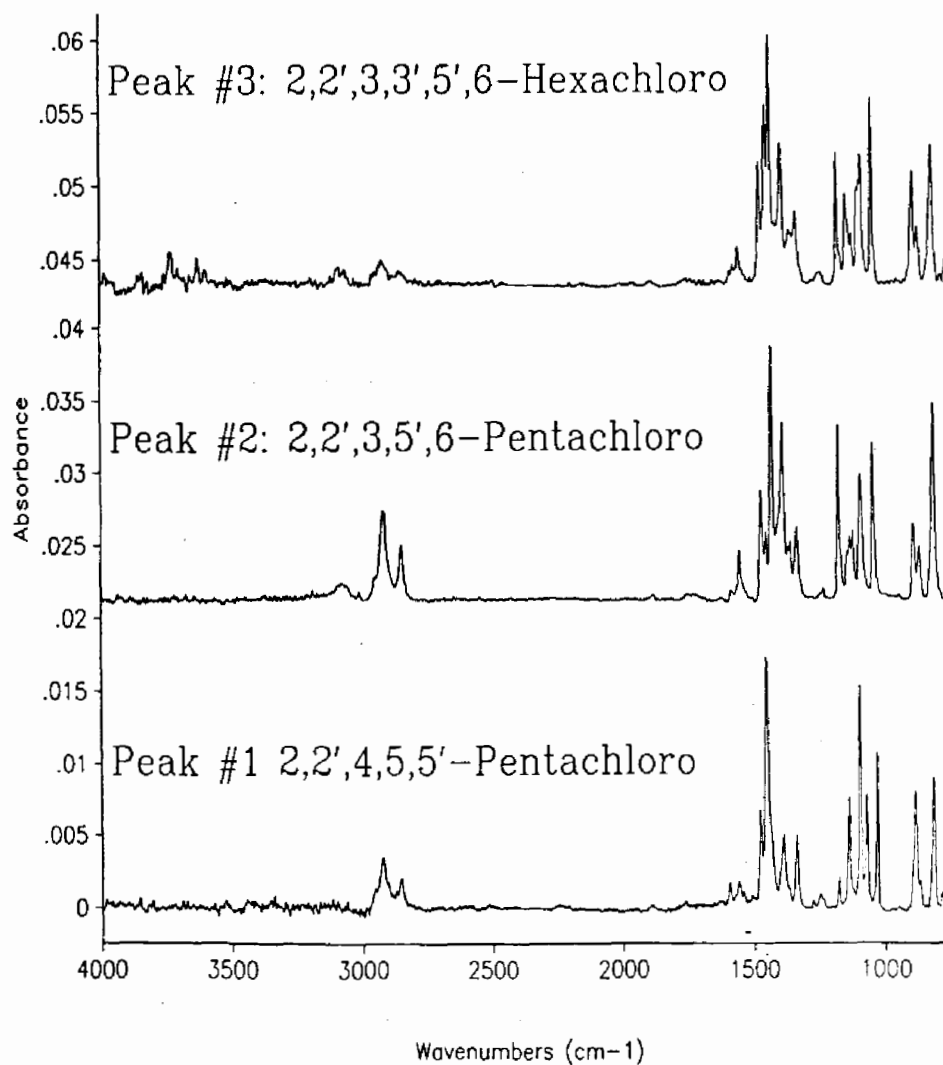


Figure 5. SFC/FT-IR spectra of the first three major peaks in the chromatogram shown in Figure 1; tentative identifications are indicated above each spectrum.

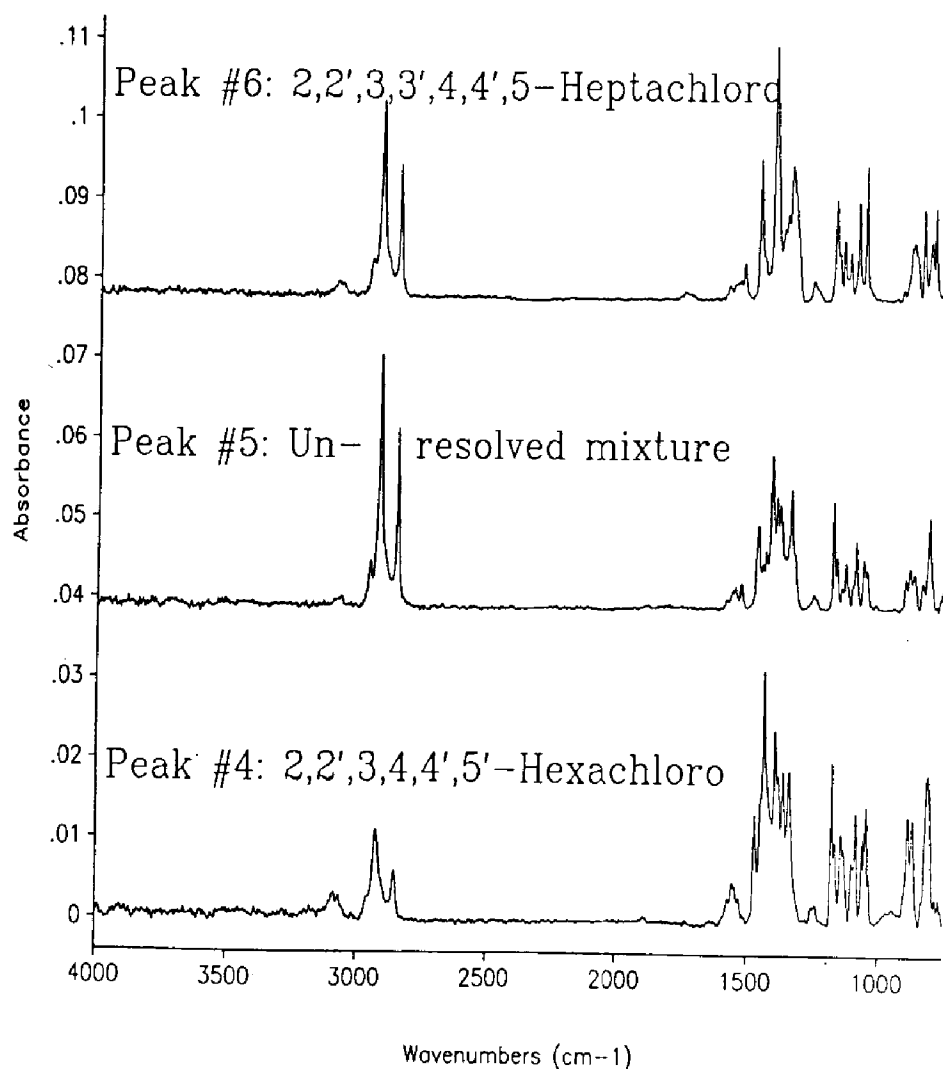


Figure 6. SFC/FT-IR spectra of the last three major peaks in the chromatogram shown in Figure 1.

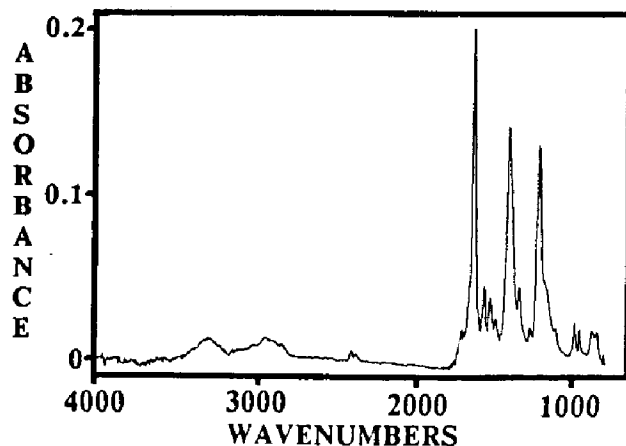


Figure 7. "FIA"/FT-IR spectrum of 60 ng of methyl violet 2B after elimination of mobile phase (100% water) at a flow rate of 50 μ l/min.

QUANTITATIVE SUPERCRITICAL FLUID EXTRACTION/SUPERCRITICAL FLUID CHROMATOGRAPHY FROM AQUEOUS MEDIA

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Supercritical fluid extraction using CO₂ has been used to extract various analytes from aqueous media. Both static and dynamic extraction modes are reported. The rate of extraction is shown to be a function of not only the density of the supercritical fluid but also the ionic strength of the aqueous media. A new scheme for trapping of analyte onto a solid phase by both cryogenic and adsorption mechanisms is described. The new scheme shows marked improvement over simple trapping into a liquid solvent. The recovery of phenol from water at the 20 ppm level is reported as 80% with an RSD of 9%.

Introduction

To date most of the work which has been done with supercritical fluid extraction (SFE) has centered on the extraction of analytes from solid, insoluble or slightly soluble matrices¹⁻⁴. Experimentation, however, is needed on systems where undesired soluble matrix components are present. King² has noted that it may be possible to isolate low levels of analytes from interfering matrix components by precisely controlling the extraction pressure. For example, he has shown that most of the DDT can be removed from lipids if the extraction is preformed at approximately 100 atm. A wet matrix will obviously be a problem in CO₂ dynamic extractions even though water is soluble in supercritical CO₂ to only approximately 0.1 %. Over time extracted water can cause restrictor plugging, and modification of the deposition and/or chromatographic solid phase. If the accumulator is a nonpolar liquid phase, the presence of water in the extract can result in a two-phase system.

Previous work in the area of extracting material from wet or liquid media has involved essentially conventional supercritical fluid extraction techniques employed on dried (freeze dried or heated) or trapped material (by solid phase extraction). Methods of this type are useful in cases where the analyte is (a) weakly retained, (b) not extremely volatile, and (c) soluble in a SF. Extraction of analytes from the raw sample using SFs, however, might prove useful in cases where the aqueous phase is hostile to direct injection onto a chromatographic column or to clean up by solid phase extraction. In addition, thermally labile materials, irreversibly retained materials, as well as polar materials with high water solubility which consequently do not solid phase separate well, may be better extracted from the aqueous matrix. Hawthorne et al.⁵ have reported that split SFE-GC (cryotrap = 5° C) allows the analysis of wet samples, in contrast to on-column SFE-GC where ice formation is a problem. In the split mode, depressurization of the SFE effluent occurred in the heated injection port. SFE-GC-MS analysis of wet fuel contaminated sediment (20 % water by weight) has been reported. The application of this SFE-GC technique was limited to the n-octane and higher boiling point species when wet samples were analyzed.

The extraction of aqueous samples with SF CO₂ is currently being studied in our laboratory⁶. Preliminary findings have been recently communicated. We describe here additional results which employ both dynamic and equilibrium extraction modes. Concurrent with our research efforts have been the reports of a similar system for the extraction of cholesterol from water⁷ as well as a segmented-flow system for on-line liquid/SFE of aqueous matrices⁸.

Experimental

The extraction vessel currently in use was acquired from Suprex Corp. (Pittsburgh, PA) and was 1 cm I.D.. x 10 cm in

length (8 ml volume). The supercritical CO₂ (Scott Specialty Gas, Plumsteadville, PA) was delivered to the extractor and any subsequent chromatography was done with a Suprex SFC 200 (Suprex Corp., Pittsburgh, PA). The equilibrium extraction system has been previously reported⁶.

SFE of the aqueous matrix followed by deposition of the analyte onto a solid phase extraction tube as well as directly into solvent was also done. A flame ionization detector heating block from a Suprex SFE 50 was modified so that a standard solid phase extraction (SPE) tube (Analytichem International, Harbor City, NJ) could be mounted on what would normally have been the flame jet (Figure 1). Nitrogen was plumbed in through the hydrogen inlet to provide a stream of heated gas to ensure that the pulled restrictor tip would not ice-up and possibly foul.

The outlet restrictor was pulled so that at 150 atm a flow of 2 ml/min of SF was sent through the extraction vessel. Unless otherwise noted the extractions were performed with a total flow of 30 ml of supercritical CO₂. Once the SFE was complete the analyte was eluted from the SPE tube with 4 ml of 50/50 MeOH/Water. For collection into a solvent a slower flow was used, 0.6 ml/min at 150 atm, and the restriction was fed directly into a sample vial containing 5 ml of 50/50 MeOH/water.

Liquid chromatography was performed with a LC/9560 ternary pump (Nicolet, Madison, WI) equipped with a TriDet UV 254 detector (Perkin-Elmer).

Results and Discussion

Aqueous solutions of triprolidine and pseudoephedrine were analyzed by equilibration SFE/SFC. Both triprolidine and pseudoephedrine were originally in the form of hydrochloride salts, and as salts they were expected and found to be insoluble in supercritical CO₂. In hopes of first forming and then extracting the free bases, a molar excess of tetrabutylammonium hydroxide was added to 3 ml of 1 mg/ml solutions of both compounds. SFE/SFC traces for both extracted compounds are shown in Figures 2a and 2b. The chromatographic traces show that the free bases were extractable from water with CO₂ as well as chromatographable under supercritical conditions.

While equilibrium SFE/SFC should perform well for nonpolar to moderately polar analytes, our primary goal was to analyze for highly polar materials. In this regard, several problems arose from poor elution behavior of the extracted analytes using 100 % CO₂.

Trapping systems which would allow for the isolation of analytes were therefore developed. Dynamic extraction was performed by decompression of the SF directly into a conventional solvent as well as being deposited onto a solid silica support as described in the Experimental section.

Figure 3 shows the effect of SF density upon the extraction behavior of phenol from water. At low density phenol is seen to be extracted quite slowly from water. After 30 ml of CO₂ were passed through the cell only 17% of the phenol was extracted. Much greater quantities of phenol could be extracted at higher density using the same amount of SF (60% extraction at 150 atm and 50° C). These numbers were obtained using deposition directly into a conventional solvent.

The major problems associated with both forms of collection (liquid and silica) arise from the large volume of gas which is produced on the low pressure end of the restrictor. A compressed flow of 1 ml/min corresponds to 100-500 ml/min of decompressed gas, depending upon the density and nature of the SF used for the extraction. Collection of the analyte into a liquid solvent consequently was especially difficult. Violent bubbling of the liquid solvent by the gas caused sporadic loss of analyte. This was evident as the extraction efficiency for phenol out of water (150 atm, 50° C with 30 ml of CO₂ used) was found to be 60% with relative standard deviation of the extraction at 15% at the 400 ppm level. Even faster flow rates are desirable as they allow for faster extractions to be run, because a greater volume of fluid can be put through the extraction vessel in a given amount of time.

Deposition of the analyte onto a solid support was intended to remove the problem of loss of the analyte due to violent bubbling solvent. Before an extraction was carried out, the effect of two different size restrictors upon the resulting temperature of the solid support trap were investigated. By use of a thermocouple installed in the dead volume of the SPE tube, it was determined that a 25 μ m capillary, providing a condensed flow of 0.5 ml/min at 350 atm, cooled the dead space to -10° to -15° C. A 50 μ m capillary provided 2 ml/min and cooled the dead space to -30° to -35° C. The 50 μ m capillary obviously allows for a faster extraction and the increased flow also cools the head of the trap more efficiently. It was therefore hoped that the added cooling would allow the SPE tube to also act as a cryogenic trap, thus providing two mechanisms for the trapping of analytes.

The solid trapping system indeed provided a significant improvement over collection of analyte into a solvent. At 20 ppm, phenol was found to be extractable to 80% (16 μ g) with 30 ml of supercritical CO₂ (150 atm and 50° C). RSD of the entire method, including the chromatography was determined to be 9%. The extractable amount of phenol was confirmed by observing the amount of phenol left in the raffinate (4 μ g with an RSD of 20%). The SFE/SFC of phenol from 6 M sulfuric acid with collection in water was carried out. It represents the case of an analyte in an aqueous environment which is hostile to many forms of clean up as well as analysis. A representative trace for the separation of the extracted phenol is shown in Figure 4.

CONCLUSION

Clearly much additional work is needed to perfect liquid/liquid extraction. Extension to a wider range of analytes including highly basic compounds is desirable. Reproducible and quantitative extraction/analysis at low ppb levels should be demonstrated. The feasibility for on-line SFE/SFC for trace analysis should be established. However, based on research to date the potential of the liquid/fluid extraction is encouraging.

ACKNOWLEDGEMENT

Financial support from the U.S. Environmental Protection Agency and B.P. America is greatly appreciated.

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FIGURES

Figure 1

Modified flame ionization heating block for the deposition of analyte onto a solid support.

Figure 2a

Tripolidine chromatographic trace.

Figure 2b

Pseudoephedrine chromatographic trace.

Figure 3

Extraction of 95 ppm phenol as a function of the amount of SF used for the extraction.

Figure 4

Chromatographic trace of phenol extracted from 6 M Sulfuric acid.

Figure 1

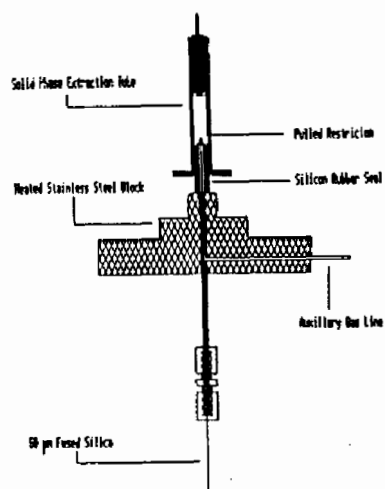
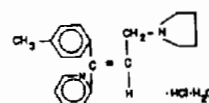
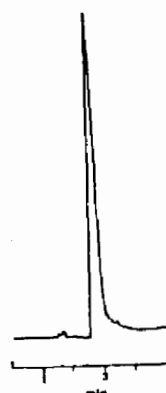


Figure 2



Extraction:

Temperature: 50°C
Pressure: 340 bar
Loop: 20 μ L

Chromatography:

Column: DELTASORBTM CN
Temperature: 60°C
Pressure: 300 bar
Flow:
2 mL/min CO₂ Constant
150 μ L/min MeOH/TEAH for 1.0 min.
150 to 450 μ L/min in 3.0 min.
450 μ L/min. Hold
Detection: 290 nm

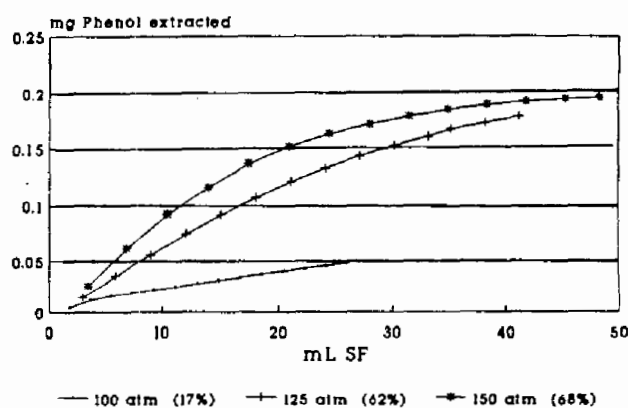
Figure 2b



Pseudoephedrine HCl
Extraction:
Temperature: 50°C
Pressure: 5000 psi
Loop: 20 μ L
Chromatography:
Column: Deltabond CN
Temperature: 60°C
Pressure: 300 bar
Flow: 2 mL/min carbon dioxide
150 μ L/min MeOH/TEAH
Detection: 254 nm

Figure 3

Wt Phenol vs Volume SF



0.286 mg Phenol total

Figure 4



Extraction:
42 ppm phenol in 6M H₂SO₄
3ml extraction
100 atm 50°C
30 minutes
Chromatography:
50/50 MeOH/water
1 mL/min
UV 254
Keystone CS 250 x 4.6mm

THE USE OF SUPERCRITICAL FLUID EXTRACTION (SFE) IN THE ANALYSIS OF ENVIRONMENTAL CONTAMINANTS ISOLATED FROM COMPLEX MATRICES

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In this study the HP 7680 Supercritical Fluid Extractor (SFE) was used to extract urban dust and soils under a variety of conditions. The extracted analytes were analyzed using the HP 5890A Gas Chromatograph with a variety of detectors, including mass selective detectors (MSD), and the results compared with those from previously used extraction techniques.

Extraction efficiencies are greatly affected by sample matrix. The interactions of environmental contaminants and sample matrices, such as density, modifier type, and modifier amount, were studied to optimize conditions for maximum recoveries.

Introduction

Analyzing complex matrices for the presence of environmental contaminants is the primary concern of many industrial- and environmental-testing laboratories. Current methods are often complicated and time consuming, involving numerous steps. The need for alternate sample preparation techniques eliminate the use of chlorinated solvents and reduce extended extraction times may be met with supercritical fluid extraction.

SFE is a rapid, clean, reproducible sample preparation technique that replaces the many labor-intensive steps of current sample preparation techniques and greatly reduces the potential for human error. Advantages of SFE include decreased sample preparation time, short extraction time, reduced analyte decomposition, and ease of use. In addition, the supercritical extraction parameters may be fine-tuned to maximize extraction efficiencies.

Experimental Methods

The conditions for the extraction of the the various samples are given in table I.

Table I. Supercritical Fluid Extraction Parameters

<u>Instrument HP 7680</u>				
Sample ID	CO ₂ Density (g/ml)	Flow (ml/min)	Temp (°C)	Time (min)
<u>Urban Dust (SRM 1649)</u>				
UD1	0.25	1.0	40	15
UD2	0.45	1.0	40	15
UD3	0.60	1.0	40	15
UD4	0.90	1.0	40	15
<u>Marine Sediment (SRM 1941)</u>				
MS1 + Hexane	0.25	1.0	40	15
MS2 + H ₂ O	0.90	1.0	40	15
<u>Spiked Soil</u>				
S1	0.85	4.0	40	40

For comparison, the spiked soil sample was extracted with a Soxhlet apparatus. The solvent used was methylene chloride, and the sample was extracted by Soxhlet for eight hours.

The gas chromatographic conditions are given in table II.

Table II. Gas Chromatographic Conditions

<u>GC: HP 5890A Series II</u>	
<u>Flame Ionization Detector</u>	
Detector Temperature	350°C
Injection Port	On-column, Oven Track on
Constant Pressure Mode	Initial Pressure, 4.6 psi
Column	25 m, 530 µ, HP-5
Oven Program	40°C (2min), 10°C/min to 350°C (5min)
Injection Volume	1 µl
Data System	HP 3365
<u>Mass Selective Detector</u>	
Mass Range	10 to 800 amu
Transfer Line	280°C
Data System	HP 9836C (Rev 3.1.1.)
Column	50 m, 320 µ, HP-5
Injection Port	On-column, Oven Track on
Constant Pressure Mode	Initial Pressure, 17 psi
Oven Program	70°C (0.75min), 30°C/min to 160°C (0.75), 5°C/min to 280°C (3.75)
Injection Volume	1 µl

Results

Using several densities, the extraction results of urban dust (SRM 1649) are shown in figures 1 to 3. These analyses were performed on the GC/MS, allowing the monitoring of the polynuclear aromatic ions. The polynuclear aromatic compounds can be extracted at various densities, depending on their molecular weight, as shown in figure 4. As the densities increase, greater amounts of hydrocarbons are also extracted from the urban dust, as illustrated in figure 5. This is a composite of the results of the analysis of supercritical extracts by GC/FID. These data indicate the importance of density in efficient extractions.

Modifiers may be added directly to the thimble containing the CO₂ or to the sample. The effects of modifier addition may be to decrease the density at which a particular analyte is extracted. This effect is shown in experiments with marine sediment and modified CO₂. In these experiments CO₂ modified with hexane, 5% by weight, was used as the extraction fluid. Experiments with CO₂ alone resulted in limited extraction of hydrocarbons or polynuclear aromatics even at high densities. As illustrated in figure 6, densities of 0.25 g/ml with modifier had increased extraction efficiency. The addition of water, which acts as a modifier, was added to the sample such that the sample was saturated. Figure 7 shows the result, which was to inhibit the extraction of an analyte from marine sediment.

The comparison of Soxhlet extraction and supercritical extraction of polynuclear aromatic compounds from spiked soil is illustrated in figures 8 and 9.

Conclusion

This study indicates the feasibility of supercritical extraction in the preparation of samples. Hydrocarbons and polynuclear aromatic compounds were extracted from urban dust, marine sediment, and spiked soil. These experiments show the importance of density, modifier type, and modifier amount in the extraction of a particular analyte from a complex matrix. Further studies are in progress to optimize the extraction conditions.

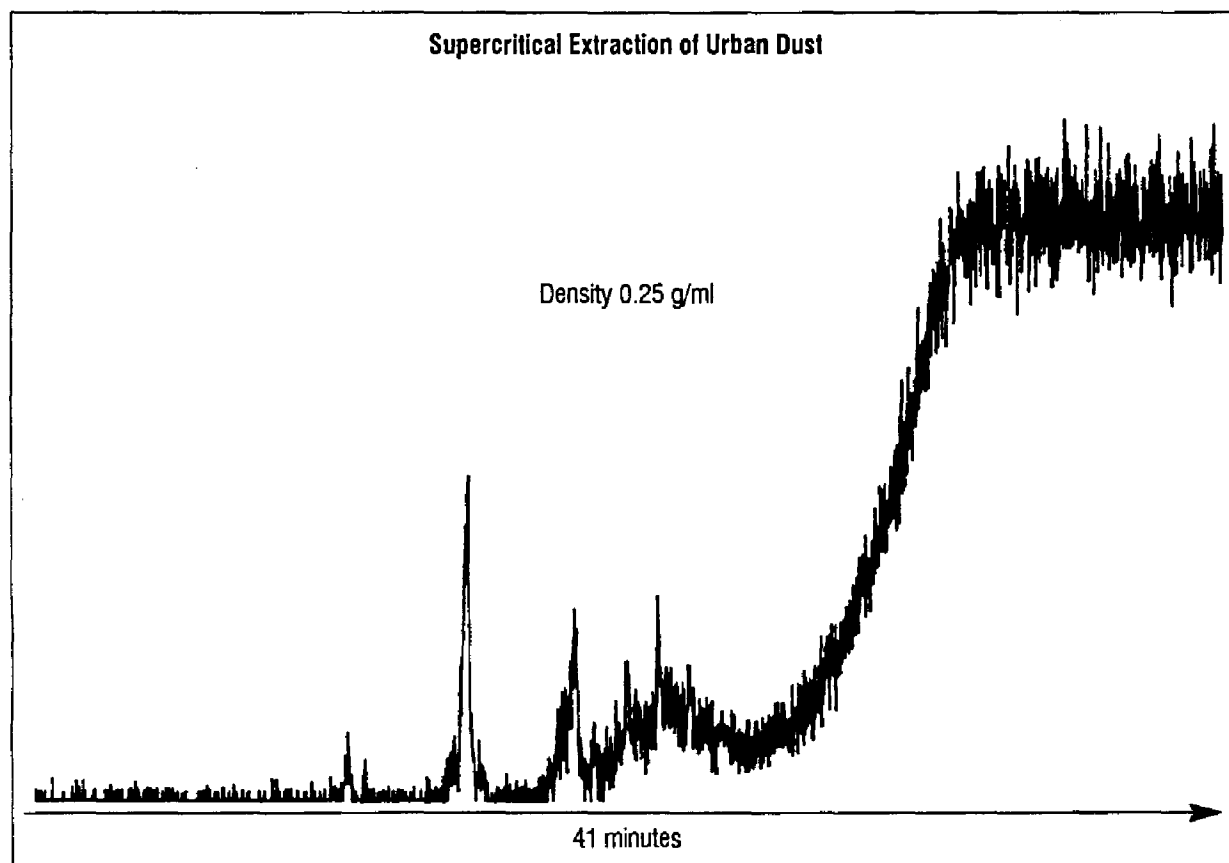


Figure 1. Total ion chromatogram for sample UD1.

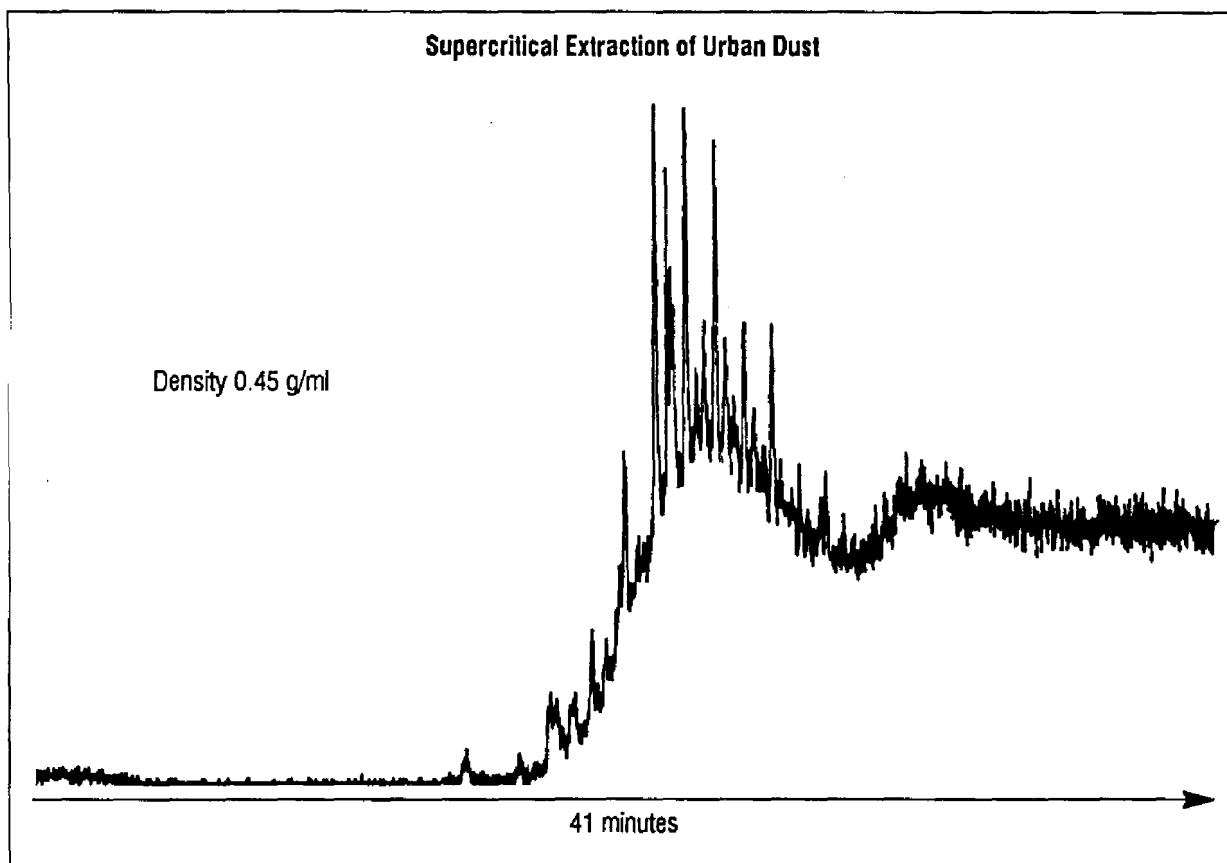


Figure 2. Total ion chromatogram for sample UD2.

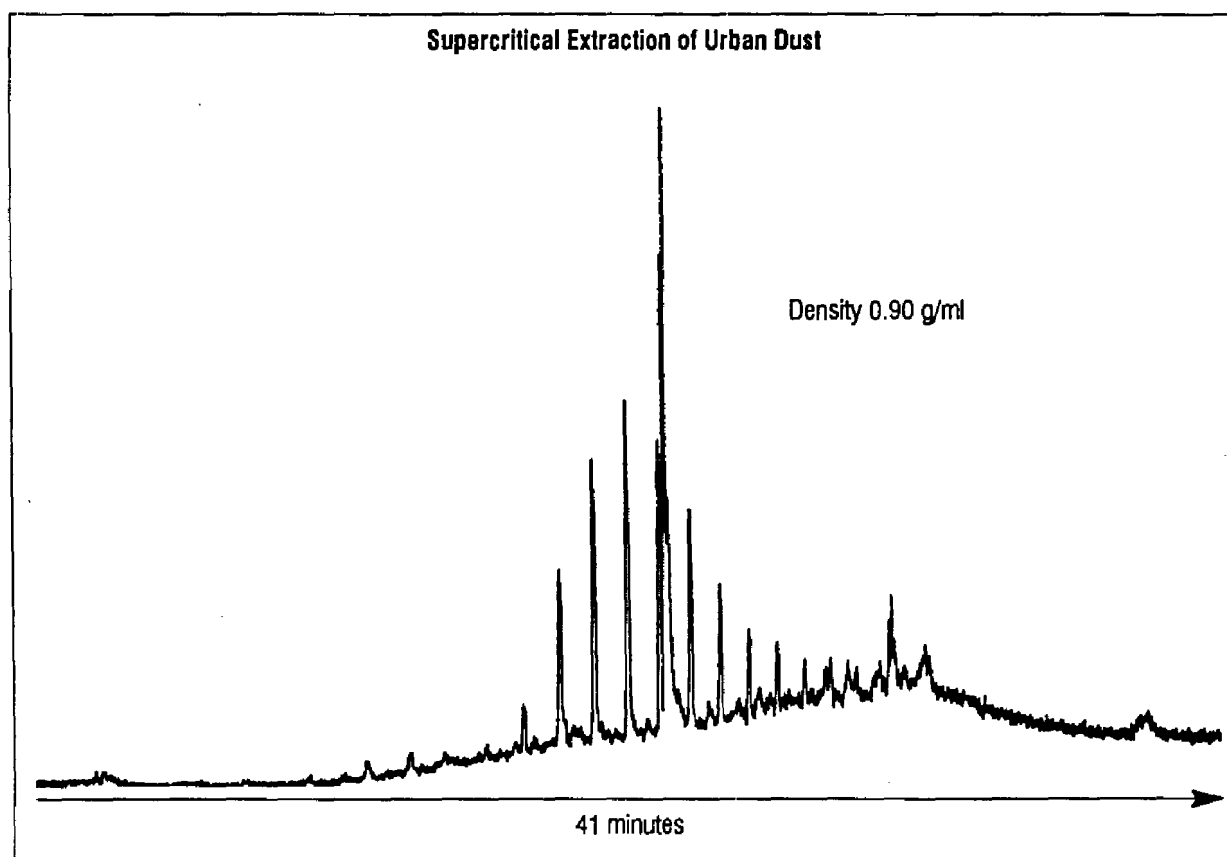


Figure 3. Total ion chromatogram for sample UD4.

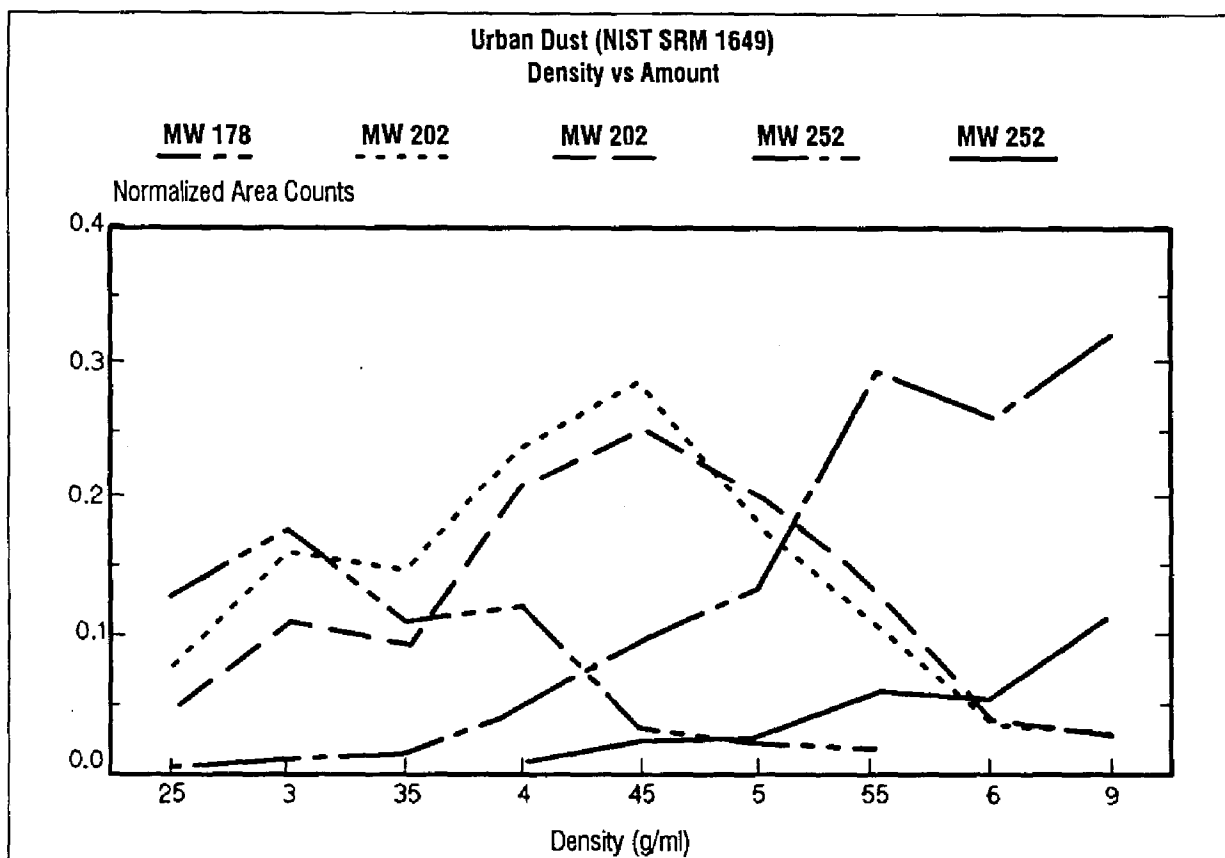


Figure 4. Comparison of the amounts of five polynuclear aromatic compounds vs extraction density.

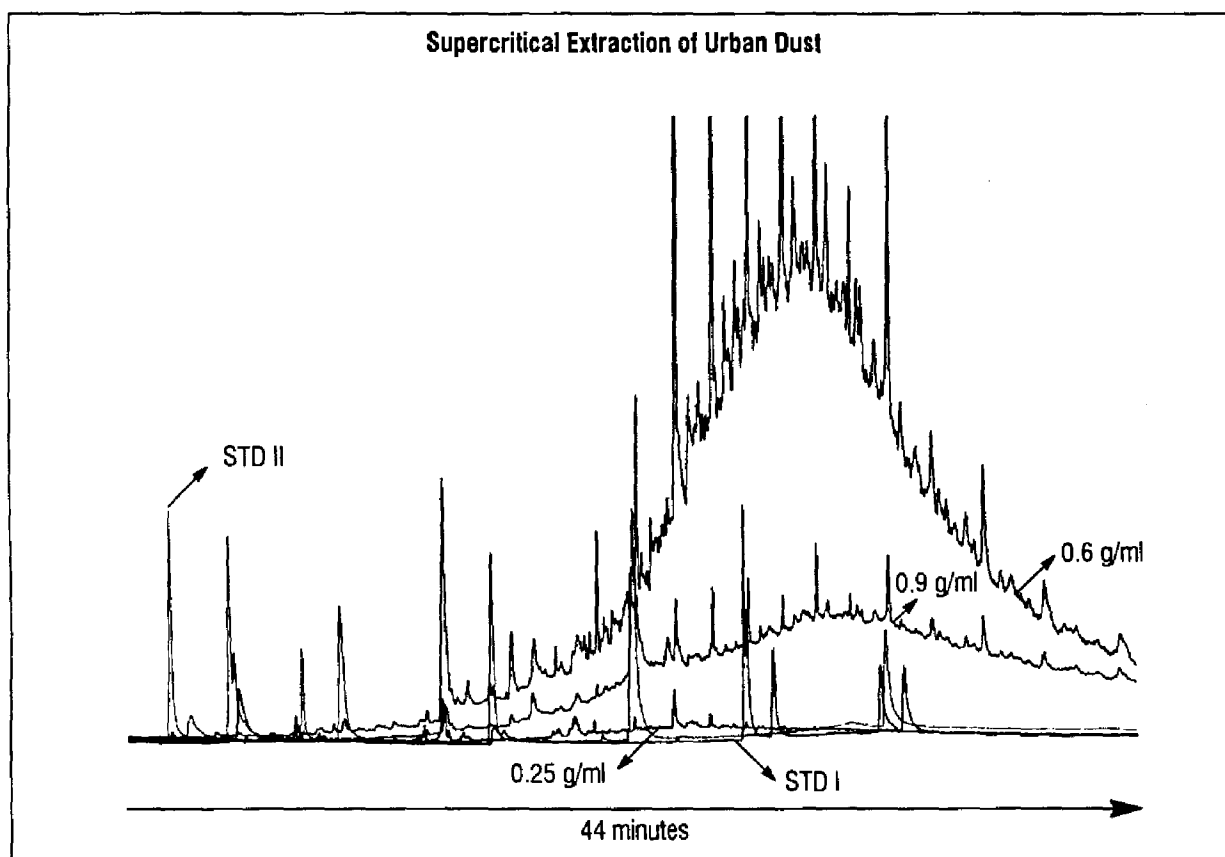


Figure 5. Merged FID chromatograms for samples UD1, UD2, UD3, and UD4.

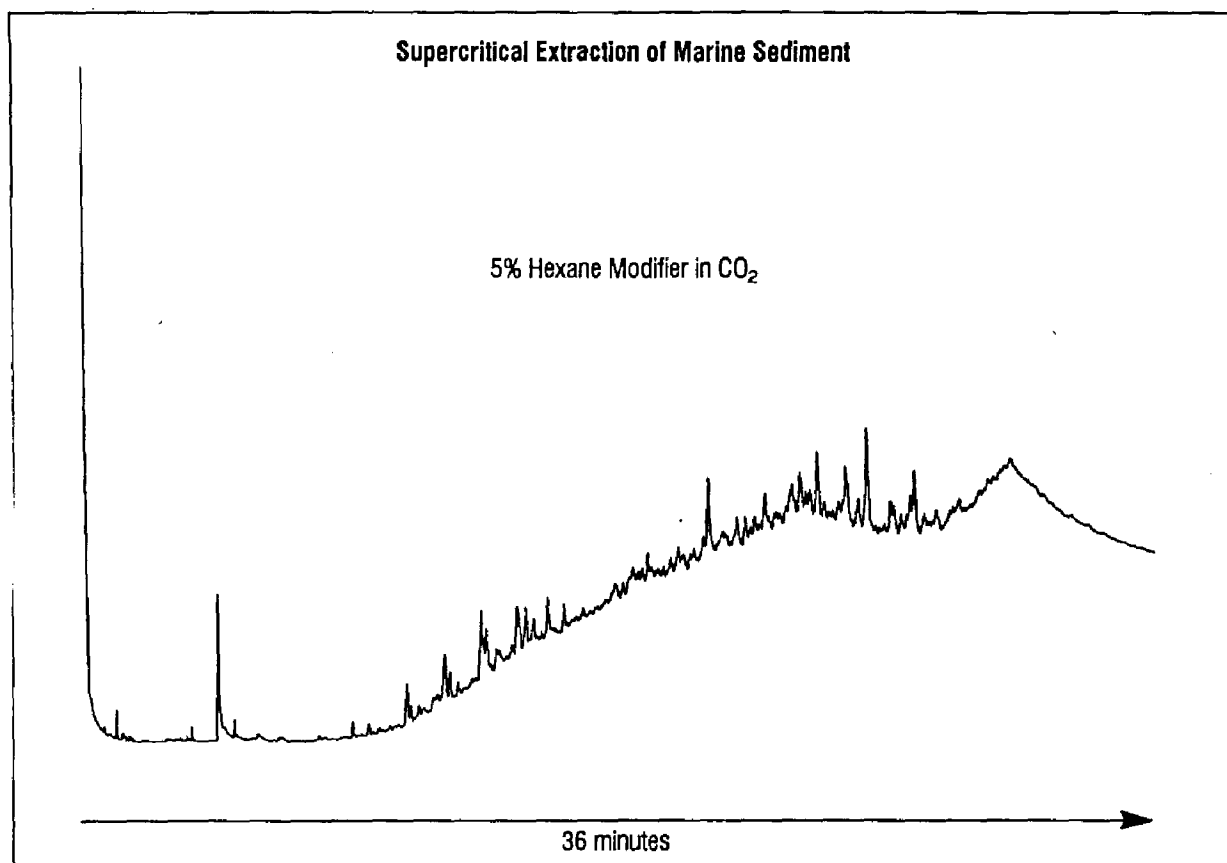


Figure 6. FID chromatogram for sample MS2 plus hexane.

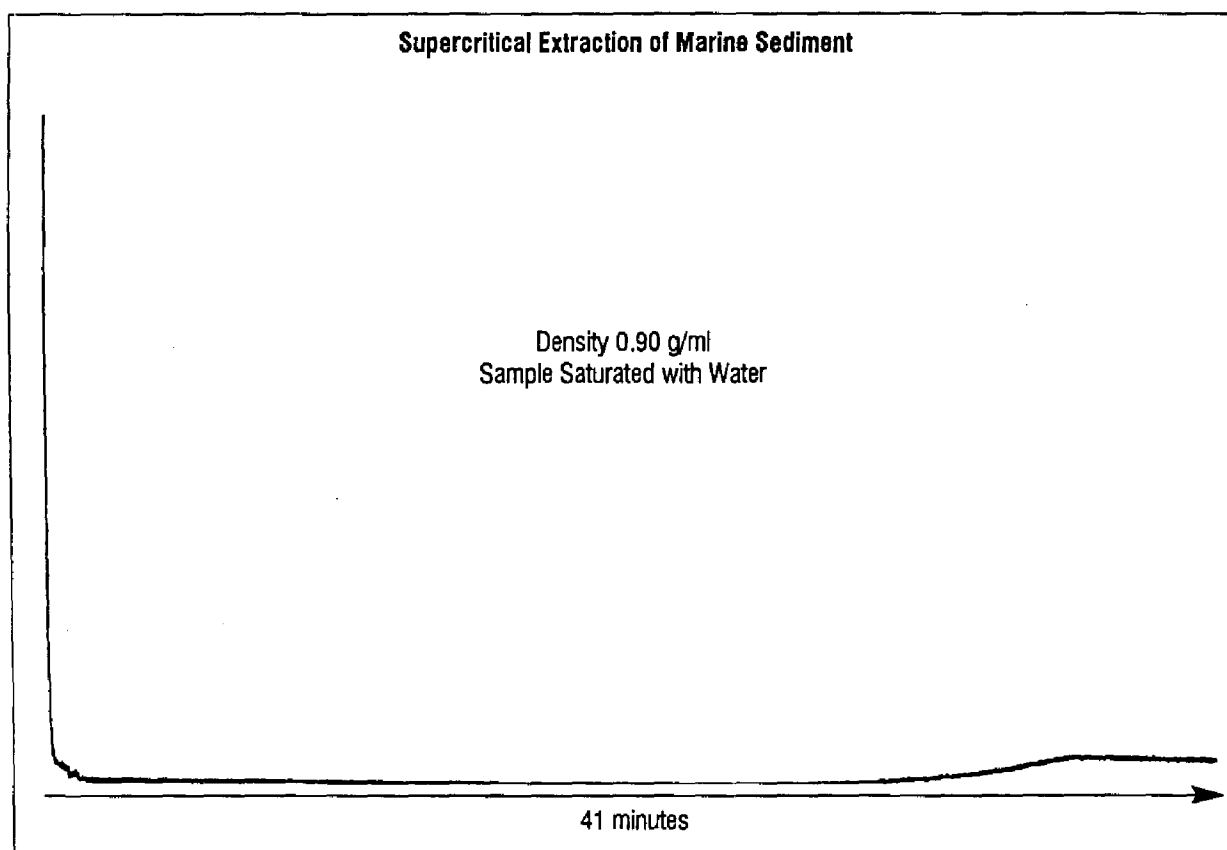


Figure 7. FID chromatogram for sample MS2 plus H₂O.

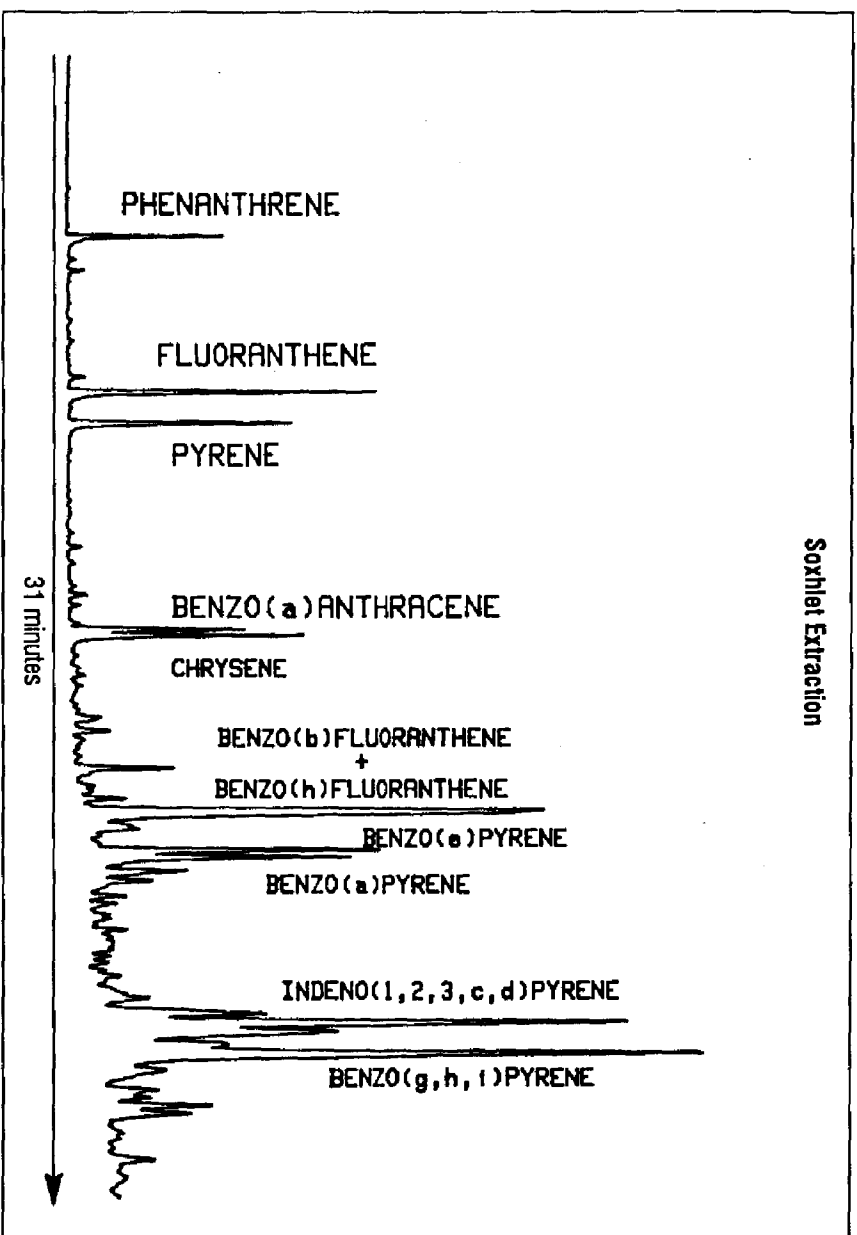


Figure 8. Total ion chromatogram for Soxhlet extraction of spiked soil.

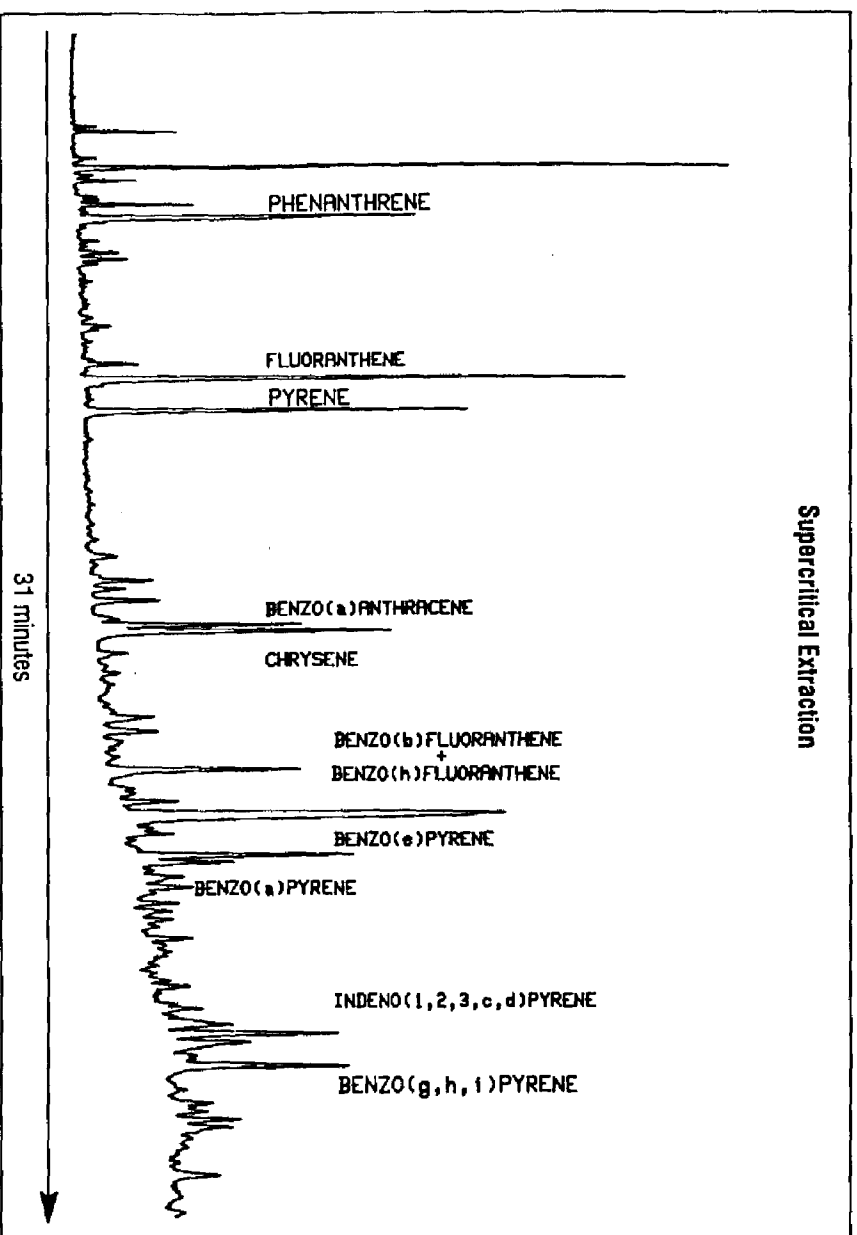


Figure 9. Total ion chromatogram for sample S1.

Indirect Supercritical Fluid Extraction of Polychlorinated Dibenzo-p-Dioxins from Rainwater and Other Aqueous Matrices

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Modified solid phase extraction (SPE) procedure for isolation of organic contaminants present in aqueous samples is described. The organic solvents commonly used in the desorption step of SPE methods are replaced by the use of supercritical fluids. The water analysis procedure uses a 10 port valve to direct the flow of aqueous sample and supercritical fluid through the adsorbent. Simple automation of the device can be achieved through an electronic actuator and microprocessor based controller. Water samples spiked with various chlorinated aromatic compounds were analyzed by supercritical fluid desorption from various adsorbents, including Tenax-GC, Octadecyl C-18, paper pulp, activated carbon, Florisil, and Amberlite XAD-2 resin. The extraction efficiencies of the adsorbed species from the sorbents using nitrous oxide and carbon dioxide was investigated. Class fractionation of complex samples is possible using density programming, and/or the stepwise use of different supercritical fluids and/or modifiers. The application of supercritical fluids to ultra-trace analysis is possible, since all the extracted compounds can be deposited at the front of a chromatographic column¹. A novel method of supercritical fluid delivery based on a thermal pump is described. The design is simple and inexpensive to assemble. Its pressure stability is dependant on the type of pressure controller used. An inexpensive comparator system gave stability of $\pm 2\%$ at 6000 PSI.

Introduction:

Environmental contaminants such as chlorinated aromatic hydrocarbons are accumulated and transported in the atmosphere, and then released into the environment by precipitation. It is necessary to develop rapid, cost-effective and accurate methods for monitoring rainwater pollutants to protect the environment and the population.

Current methods used to analyze organic contaminants in aqueous samples involve liquid-liquid extractions or adsorption onto sorbents followed by solvent desorption. These methods are generally time consuming and labour intensive. Also, they often involve the use of high purity and expensive solvents such as benzene and dichloromethane. With growing concern over occupational health and safety, an alternative to the use of such organic solvents is desirable. A further disadvantage of these traditional techniques is the difficulty in automating the process.

To improve this situation, solid phase extraction (SPE) procedures have been developed. The instrumentation associated with these techniques is based on cartridges filled with material similar to column packings used in solid chromatographic columns, and uses chemically modified silica^{2,3}. The primary advantage of SPE is the reduced consumption of high purity solvents, thereby reducing analysis cost and the need for solvent disposal. The time required to isolate the analyte of interest is also greatly reduced when compared to classical extraction methods. However, SPE still uses a small amount of solvent.

In this paper we present and discuss a sample isolation approach based on supercritical fluid extraction using carbon dioxide and nitrous oxide. The supercritical fluid is delivered from a new thermal pump⁴. The extraction process has been developed by chemical engineers^{5,6} and has recently attracted deserved attention by analytical chemists^{1,7-10}. This separation technique exploits the properties of the compressed gas, in most cases inexpensive and non-toxic carbon dioxide, at temperature and pressure above its critical point. The method combines both distillation and extraction in a single process since vapour pressure and phase separation are involved. The major features of a supercritical fluid extraction include: rapid extraction due to low viscosity and high diffusivity compared to liquids; selectivity of the process through density programming; and low temperature extractions of non-volatile compounds. Supercritical fluid extraction systems can be easily automated since the transfer of the analyte can be accomplished by flowing the mixtures in the system and analyte separation from the fluid can be achieved by lowering the pressure.

Analytical supercritical fluid extractions have been applied to isolate organic contaminants, in most cases polycyclic aromatic hydrocarbons from solid matrices such as flyash, dust, or sorbents such as Amberlite XAD resin⁸ or Tenax GC¹. This paper describes inexpensive instrumentation and procedures which enable rapid isolation of pollutants from aqueous matrices.

Experimental Methods:

Supercritical Fluid Delivery: Supercritical fluid was delivered to these experiments by a thermal pump, based on the thermal expansion of a compressed gas⁴. The pumping system consists of a supply tank for the SF gas connected to a high pressure vessel (thermal pump) via a high pressure valve. The vessel has independent heating and cooling systems, has a pressure transducer which monitors internal pressure, and has a thermistor monitoring temperature. A rupture disk is an integral part of the safety system, and will vent the system at 7000 PSI, well below the design rating of the vessel. The extraction vessel is thermostatically controlled by an independent heater circuit. The extraction vessel is constructed of a suitable length of stainless steel tubing with Swagelok fittings at either end. Another such tube filled with activated carbon serves as a trap to remove impurities from the SF stream.

Operation of the pumping system involves cooling the pump to -15°C by flowing liquid nitrogen or carbon dioxide through a copper tube coiled around its exterior. The supply of gas is allowed to fill the vessel and condense, increasing in density as the temperature decreases. After the system has equilibrated at this temperature, it is closed to the gas supply tank and heated to increase its internal pressure. The amount of heat required to reach operating pressure is dependant on the initial temperature of the system. Figure 1 shows the response of the pump at various initial temperatures.

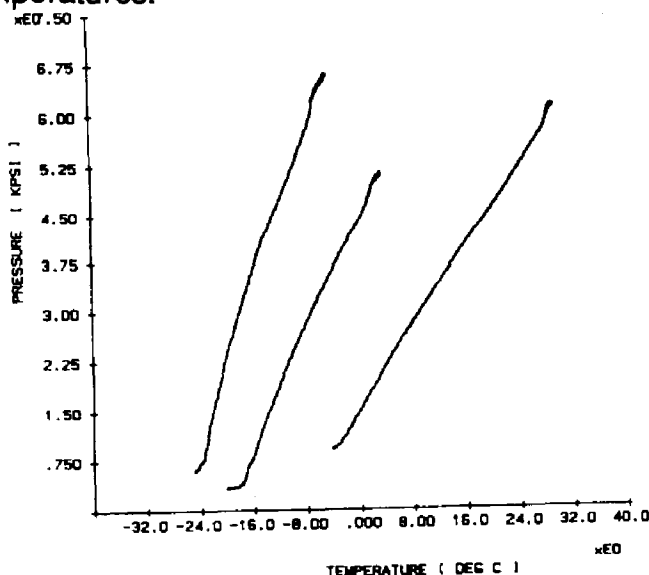


Figure 1 Thermal pump response at different initial temperatures.

As the SF is delivered, the amount of heat applied must be increased to maintain operating pressure. This has been accomplished in two ways. Initially, a simple op-amp comparator circuit was constructed (Figure 2) which switched the power to the heater on or off in response to the signal from the pressure transducer; on if the pressure dropped below the working pressure, off if it went above. There are also thermal shutdown and manual reset features, as well as variable heater duty cycle. This controller produced pressure stability of ± 200 PSI @ 6000 PSI. To improve the stability of the system, a commercial 3 mode controller (Proportional Integral Derivative - PID) (Omega Engineering) was used. This controller is infinitely tunable and has the advantage that it can be programmed to pressure ramp, analogous to temperature programming of a GC oven. This controller increased the

stability to ± 35 PSI @ 6000 PSI, or a deviation of less than 1%. There are two limiting factors on the stability of the thermal pump. The dynamic conditions in the pump during its operating cycle indicate that it can only be tuned for one set of conditions, thus the controller is only optimally tuned for a short period of time, and the tune is compromised for the remainder of the cycle. This problem, combined with the large thermal mass of the 25 lb stainless vessel cause the small oscillations in pressure.

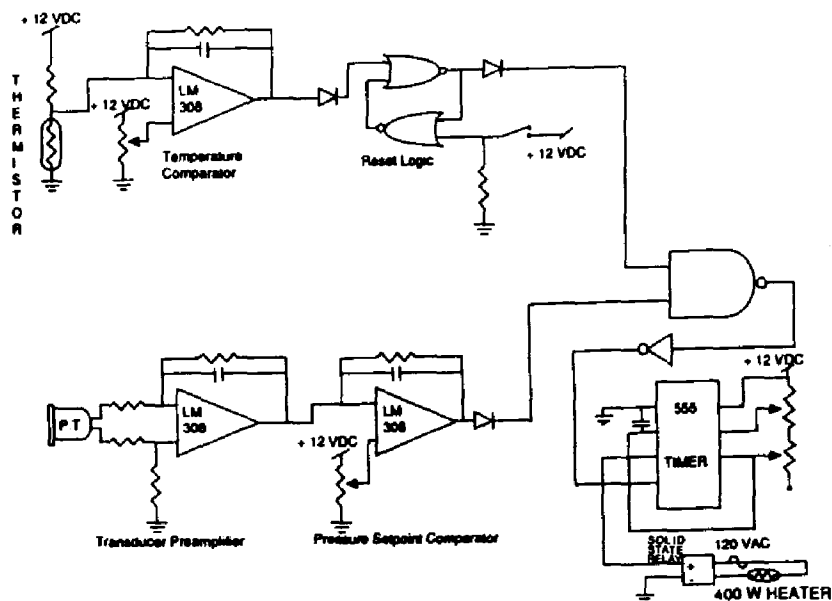


Figure 2 Simple comparator controller circuit.

In order to address the stability problem, as well as to increase the safety of the design, a low volume twin tube system was constructed from two lengths of 1/2" stainless steel pipe, fitted with valves at each end. Figure 3 schematically shows the system. With this system, which operates on the same principle as the larger pumps, a continuous supply of SF can be delivered. One stage of the pump is cooled, filled, and then heated to bring it up to pressure. As it is being operated, stage two is cooled, filled and pressurized to just below operating pressure. When stage one is nearly empty, stage two is brought up to operating pressure, and stage one is quickly cooled. The valves can be either check valves or active solenoid valves, operated at the appropriate time by differential pressure or an electronic signal from a central processor. This system is thus also easily automated.

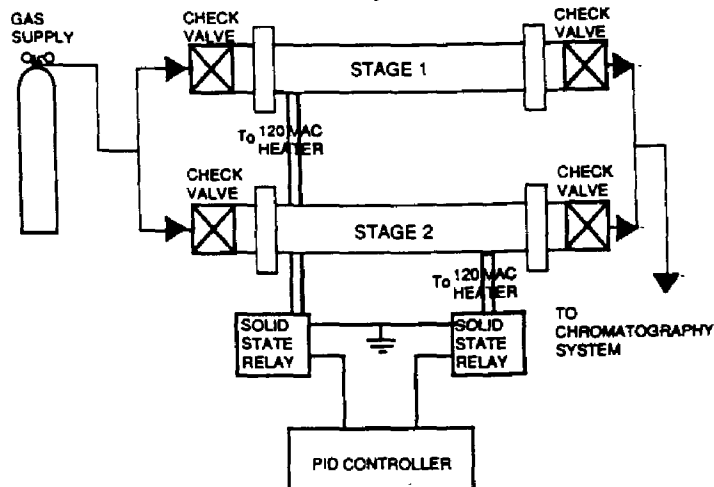


Figure 3 Twin tube low volume thermal pump.

Water Analysis System: The system to remove organic contaminants from aqueous samples was composed of a ten port valve (Valco Instruments, Houston, Texas) connected to the extraction vessel, an inlet for the water sample, a SF inlet, an exit to a waste bottle and an exit for analyte collection.

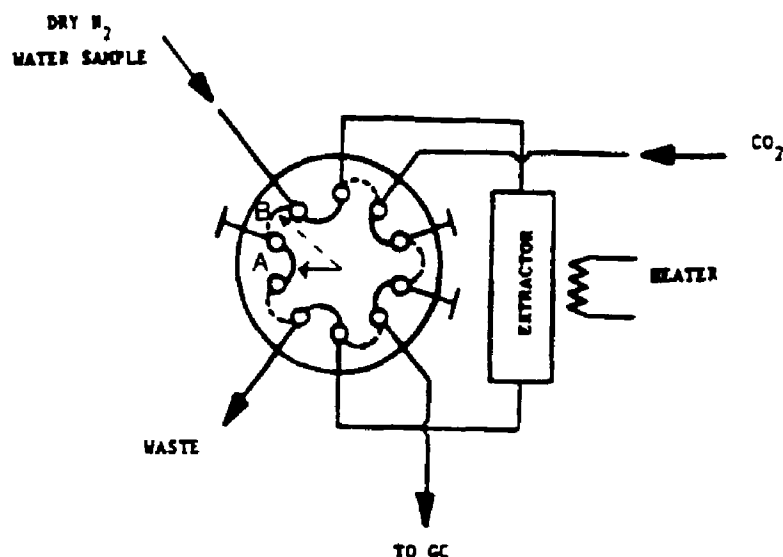


Figure 4 Water analysis apparatus.

In position A, water was forced under pressure from a dry nitrogen cylinder through the adsorbent in the extraction vessel and into the waste bottle. In this step, the organics from the water are adsorbed onto the adsorbent in the extraction vessel. After the water has all passed through the adsorbent, the adsorbent is dried by continuing to pass the dry nitrogen through the adsorbent while heating the extraction vessel. Once the adsorbent has been dried, the valve is switched to position B. The SF flows through the adsorbent in the reverse direction and desorbs the organics adsorbed in the first step. The analyte is recovered by bubbling the exiting SF into a vial containing about 1 mL hexane. The contents of the vial are then blown dry with a gentle stream of nitrogen, then brought up to 100 μ L volume with hexane and analyzed by GC-ECD.

Desorption Step Recoveries: Desorption of an OCDD standard from various adsorbents using supercritical carbon dioxide and nitrous oxide was investigated. Cartridges made from 1/4 inch stainless steel tubing and Swagelok nuts and ferrules, were filled with about 80 mg of the adsorbents. A 5.0 microlitre portion of an OCDD standard (3.114 ng/ μ L) was injected into the centre of the adsorbent bed. The standard compound was then extracted using the supercritical fluid at 400 atm for 1h with a gaseous flow rate of 120 mL/min. The extracted materials were trapped by bubbling the supercritical fluid into a vial containing about 1 mL of hexane. After completion of the extraction, the hexane was blown to dryness using a gentle stream

of dry nitrogen, then brought up to final volume in hexane. The sample was then analyzed using GC-ECD to determine OCDD concentration and extraction efficiency.

Leaching Studies: A 10 ng spike of 1,2,3,4-TCDD in hexane was injected into the centre of the adsorbent bed. A 50 mL quantity of water was passed through the adsorbent at 3 mL/min., the adsorbent was dried and then extracted using N₂O or CO₂ at 6000 psi and 50°C for 1 h. The extract was then analyzed using GC-ECD to determine whether the water had leached any of the TCDD from the adsorbent.

In-Flow Injection: A T-union was connected to the entrance of the extractor, the water inlet was connected to one port of the T-union and a septum was placed in the other port of the T-union. While water was being forced through the extractor, a syringe was used to pierce the septum and inject a 10 µL spike of the 1,2,3,4-TCDD standard (prepared as 1 ng/µL in MeOH) into the flow. The adsorbent filled extractor was dried and extracted to determine extraction efficiency against an external standard using GC-ECD.

Analysis of Spiked Water: The 50 mL water sample was spiked with 10 µL of a 1 ng/µL solution of 1,2,3,4-TCDD standard in MeOH. The water was then placed in an ultrasonic bath for 10 minutes to facilitate dissolution. The concentration of the dioxin in the water was 0.2 parts per billion (ppb) which is 1/3 of the solubility reported by Schler et. al.¹⁰. The water was then forced through the adsorbent-filled extractor at a flow rate of approximately 3 mL/minute, then the extractor was dried and extracted. The extraction efficiency was determined using GC-ECD and an external standard.

GC Analysis: All of the analyses were done on a Varian 3400 gas chromatograph equipped with an electron capture detector (ECD), a septum programmable injector (SPI), and a 30m X 25µm DB-5 capillary column (J&W Scientific, California). The analyses were carried out using an external standard method. Each time a spike of an adsorbent or water was done, an identical aliquot of the standard was injected into a vial, evaporated to dryness and diluted to 100 µL. A 0.5 µL injection of this standard is then analyzed, using the peak area of the compound in the standard as 100% recovery.

Fractionation Studies: The Tenax filled extractor was spiked with a mixture containing tetrachlorobenzene, hexachlorobenzene, trichloro-PCB, pentachloro-PCB, 1,2,3,4-TCDD and OCDD. Extractions were attempted with CO₂ and N₂O at various pressures to determine whether class-selective fractionations could be done.

Discussion and Results:

The development of a method for extraction of polychlorinated dibenzo-p-dioxins from water proceeded in a series of steps. Initially, the ability of supercritical N₂O and CO₂ to desorb dioxins from a number of different adsorbents was

investigated. An OCDD standard was chosen as the standard to be spiked onto the adsorbents because it is expected to be the most difficult to extract due to its low solubility. It was assumed that if this particular dioxin isomer could be desorbed then all of the others should also be able to be desorbed. The extractions were performed at 400 atm and 50°C and the extract was collected for 1 h. Table I illustrates the results achieved.

These results indicate that N₂O is a more efficient supercritical fluid for the extraction of dioxins from these adsorbents. A strong matrix effect is also evident, since the OCDD was desorbed well from Tenax GC, the octadecyl phase and pulp but very poorly desorbed from activated charcoal, florisil and Amberlite XAD-2. Obviously, the OCDD is much more strongly bound to the latter group of adsorbents.

Table 1 Extraction of OCDD

Adsorbent	Carbon Dioxide % Recovery \pm 10%	Nitrous Oxide % Recovery \pm 10%
Tenax GC	35	95
Octadecyl (C ₁₈)	92	100
Activated Charcoal	ND	ND
Florisil	ND	10
Amberlite-XAD2	ND	ND
Pulp	80	92

ND-none detected
 -extractions done for 1hr.
 at 6000psi. and 50°C

Based on these results, continuing experiments were limited to Tenax-GC and octadecyl extracted with N₂O and pulp extracted with CO₂. Pulp is not a common adsorbent, but in other experiments conducted in the laboratory, it was noted that dioxins were easily desorbed from pulp. Therefore, pulp was considered for use as an adsorbent.

The second step of the research was to determine which adsorbents would adsorb dioxins from water. In these experiments, a 1,2,3,4-TCDD standard was used instead of the OCDD. The TCDD standard is much more water soluble than OCDD (more than 1000 times more soluble)¹⁰ and therefore it was much easier to extract a detectable quantity. Initially, water leaching of the TCDD from the adsorbents was examined. A direct spike on the adsorbent was followed by passing water through the adsorbent. The adsorbent was then extracted to determine if any leaching of the TCDD had occurred. Three replicate experiments were done and deviations were calculated as shown in Table II.

Table II Extraction of 1,2,3,4 TCDD

Adsorbent	% Recovery
Tenax GC (N ₂ O)	100± 4%
Octadecyl (N ₂ O)	100± 6%
Pulp (CO ₂)	87± 3%

*extractions done at 6000 psi and 50°C for 1 h.

The excellent recoveries from Tenax-GC and octadecyl indicate that leaching is not occurring. Less than 100% recovery from the pulp is likely due to incomplete desorption rather than leaching.

In the second stage, the TCDD was spiked in the flow of water as it passed into the adsorbent bed. In this way, better simulation of the dioxin actually being dissolved in solution was hoped to be achieved. Three replicate runs of each adsorbent were done.

Table III Extraction of 1,2,3,4 TCDD

Adsorbent	% Recovery
Tenax(N ₂ O)	80± 5%
Octadecyl(N ₂ O)	85± 10%
Pulp(CO ₂)	76± 3%

* extractions done at 6000 psi and 50°C for 1 h.

The results in Table III show lower recoveries than obtained with direct spiking onto the adsorbents but this is a result of the dioxins never actually contacting the adsorbent. Due to its low solubility in water, the TCDD likely precipitates out, to some extent, at the point where it is injected into the flow of water and therefore is never able to be adsorbed and subsequently extracted. Dioxins that are dissolved in water should not encounter this problem. The final stage of this step was to actually dissolve the 1,2,3,4-TCDD in water and put this spiked water through the extraction procedure. The water was spiked at 0.2 ppb which is about 1/3 its reported solubility level¹⁰. This was done to ensure that the TCDD would not precipitate out as in the in-flow injection of the standard. Again three replicate experiments were done with each adsorbent, and deviations were calculated.

Table IV Extraction of 1,2,3,4-TCDD

Adsorbent	% Recovery
Tenax(N ₂ O)	67± 20%
Octadecyl(N ₂ O)	68± 30%
Pulp(CO ₂)	55± 20%

* extractions done at 6000 psi and 50°C for 1 h.

The results shown in Table IV illustrate significantly lower recoveries than had been achieved in other experiments. This lowering of extraction recoveries indicates a loss of analyte at some point in the system. The possibility of break-through of the TCDD in the water was investigated by re-running the same water through the system. No more TCDD was recovered so break-through is not likely. It is likely though that the TCDD is adsorbed and immobilized onto the glassware used as a water reservoir and thus was never able to reach the adsorbent. Three runs were done with each adsorbent to determine the deviation in recoveries. The water reservoir bottle was rinsed with MeOH and hexane between runs to remove any TCDD adsorbed on the glass and prevent cross-contamination. One method for compensating for the loss of analyte adsorbed onto the glassware would be the use of a ¹³C labelled internal standard. It could be assumed that the ¹³C labelled TCDD would be adsorbed to the same extent as the unlabelled TCDD. Using GC/MS one could quantitatively compensate for this adsorption effect.

A larger deviation (30%) was observed in the runs using octadecyl bonded to microporous silica as the adsorbent. Excellent recoveries were achieved with the first extraction on fresh octadecyl but the recoveries dropped as the same adsorbent was used repetitively. Stripping of the octadecyl phase by the supercritical fluid is likely occurring, leaving behind a bare silica surface which binds strongly to the dioxin and causes poorer recoveries.

The ability of supercritical fluids to do class-selective extractions or fractionate samples was investigated. A mixture of chlorinated benzenes, polychlorinated biphenyls (PCB's), and dioxins was injected directly onto the Tenax GC adsorbent in an extractor. Extractions were done with N₂O and CO₂ at various pressures and the extract was taken at various time intervals to try to separate these three classes of compounds. It was found that N₂O desorbs all of the compounds within 20 minutes and very little separation of the compounds could be achieved. Since CO₂ was found to desorb dioxins poorly from Tenax, it was tested to see if it could be used to fractionate the mixture (Table V). At 5000 psi and 50°C, 74% of the pentachloro-PCB and all of the trichloro-PCB and chlorinated benzenes were removed within 20 min. with loss of 23% of the TCDD and no loss of OCDD. At 3000psi and 50°C, 60% of the pentachloro-PCB and all of the trichloro-PCB's and chlorinated benzenes were removed after 40 min. with only a 5% loss of the TCDD and no loss of the OCDD.

Table V Class fractionation study.

Extract. Time	Extract. Pressure	³ Cl-PCB Removal	⁵ Cl-PCB Removal	TCDD Loss	OCDD Loss
20 min.	3000 psi	100%	60%	5%	0%
40 min.	5000 psi	100%	74%	23%	0%

It appears that better separation is achieved at lower pressure but the analysis time is greatly increased. Once the interferences are removed, N₂O can be used to desorb the dioxins.

Conclusions:

Solid phase extraction using supercritical fluid desorption is a good alternative for isolation of organic contaminants such as polychlorinated dibenzo-p-dioxins from aqueous samples. This process can be controlled by a single six port valve, though we used a ten port device, and can thus be easily automated. The combination of this method with direct on-column deposition of analytes by decompression of the supercritical fluid⁹ will facilitate ultra-trace analysis. In this procedure, all extracted material is injected into the column, rather than only a small fraction as is common when performing solvent extractions. Class fractionation of complex samples is possible using density programming and step-wise use of different supercritical fluids and/or modifiers. More work is needed to optimize this process. Tenax-GC requires the use of nitrous oxide as the supercritical fluid to obtain good recoveries. Quantitative extractions of dioxin can, however, be ensured with carbon dioxide if chemically modified silica or paper pulp are used as the adsorbent.

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MONITORING OF NITROGEN POLLUTANTS AT MT. MITCHELL, NORTH CAROLINA.

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ABSTRACT

Gaseous nitrogen compounds (nitric acid, nitrous acid, ammonia, and nitrogen dioxide), and particulate nitrogen compounds (nitrate and ammonium) were measured in ambient air using Annular Denuder System (ADS) and chemiluminescence nitrogen oxides analyzer at Mt. Mitchell State Park (~2006m MSL), North Carolina. Measurements were made during May through August of 1988 and 1989. Further, measurements of nitrate and ammonium in cloud water samples were also made during the same period. Concentrations of gaseous nitric acid using ADS were found to be in the range 0.13-5.62 $\mu\text{g}/\text{m}^3$ with a mean of 1.07 $\mu\text{g}/\text{m}^3$ during 1988, and in the range 0.55-2.60 $\mu\text{g}/\text{m}^3$ with a mean of 1.39 $\mu\text{g}/\text{m}^3$ during 1989. Nitric acid levels were found to be higher during the daytime compared to the nighttime levels, which are consistent with the photochemical formation of gaseous nitric acid. Gaseous ammonia levels were found to be in the range of 0.01-4.98 $\mu\text{g}/\text{m}^3$. Particulate nitrate, ammonium and sulfate concentrations were found to be have range of 0.02-0.21 $\mu\text{g}/\text{m}^3$, 0.01-4.72 $\mu\text{g}/\text{m}^3$ and 0.21-18.13 $\mu\text{g}/\text{m}^3$ for 1988, and 0.1-0.78 $\mu\text{g}/\text{m}^3$, 0.24-2.32 $\mu\text{g}/\text{m}^3$ and 0.5-11.8 $\mu\text{g}/\text{m}^3$ for 1989 respectively. The fine aerosol fraction was dominated by sulfate particles followed by ammonium particles. Mean nitrate and ammonium ion levels in cloud water samples for 1988-1989 ranged from 142-192 $\mu\text{mol}/\text{l}$ and 153-185 $\mu\text{mol}/\text{l}$ respectively. The incorporation of the pre-existing gaseous nitric acid/nitrate into the cloud is not efficient to account for the measured nitrate concentrations in the cloud water.

INTRODUCTION

Air pollution is thought to be one of the contributing factors for the high elevation forest decline in the eastern United States (Cowling, 1985; Woodman and Cowling, 1987). High amounts of acidic deposition and elevated levels of gaseous atmospheric photochemical oxidant pollutants (e.g., ozone, hydrogen peroxide) have been observed at Mt. Mitchell State Park, (Mt. Mitchell, elevation ~2038m MSL), North Carolina. Mt. Mitchell is the highest peak east of the Mississippi river. Ozone, a photochemically formed secondary pollutant has been observed at levels exceeding the National Ambient Air Quality Standards (NAAQS) (Aneja et al., 1990); and has frequently been >50 ppbv during the growing season (May through September) which could cause damage to plants (Mohnen and Cowling, 1988). Significant quantities of acidic substances are also found to deposit on the canopy which may contribute to the observed decline in the ecosystem.

Greater than normal atmospheric deposition of nitrogen compounds is thought to be one of the likely mechanisms by which airborne pollutant chemicals could cause injury to spruce-fir forests. According to this hypothesis (Nihlgard, 1985), nitrogen containing pollutants deposited on foliage and soils could cause leaf damage; and also may extend the period of growth later into the fall, thus inhibiting the "hardening off" processes by which needles protect themselves from frost injury during the severe winter weather (Friedland 1984).

Since this mechanism involves the mineral nutrition of growing plants, and, specifically, the availability of nitrogen at a specific time in the growing season, it is important to establish the extent to which nitrogen is supplied by atmospheric exposure throughout the growing season. Thus, it is not clear whether general overfertilization or time-specific fertilization is important, or that there is, in fact, a seasonal factor in the exposure/deposition of nitrogenous air pollutants. Hence, characterization of the atmosphere for nitrogen containing species and their chemistry becomes important in exploring the forest decline phenomenon.

EXPERIMENTAL TECHNIQUES

Gas- phase measurements: Ambient gaseous nitric acid, gaseous nitrous acid, gaseous ammonia, and particulate nitrate and ammonium measurements were made during the summers (May through August) of 1988 and 1989 utilizing the Annular Denuder System (ADS) technique (Possanzini et al., 1983). Continuous gas phase measurements of nitrogen oxides (NO and NO₂) were made using a chemiluminescence nitrogen oxides analyzer. The annular denuder system used at Mt. Mitchell consisted of an impactor preseparator to remove coarse aerosol fraction (>2.5 µm), three annular denuder tubes in series to collect the gaseous species and a filter pack to collect the aerosol fraction. The first denuder was coated with 0.1% solution of NaCl to collect gaseous nitric acid to remove gaseous nitric acid from the other acidic species. The second denuder was coated with a solution of 1% glycerine and 1% Na₂CO₃ solution in a 1% mixture of methanol and distilled water to capture nitrous acid and sulfur-dioxide. The third denuder was coated with 1% citric acid in methanol for the collection of ammonia. The filter pack consisted of a teflon filter for the collection of fine particulates and a nylon filter to capture any volatilized nitric acid during the dissociation of ammonium nitrate aerosol. The denuder system was operated in a laminar mode at a constant flow rate of 16.5 l/m. Though the

measurements were primarily made for 24 hours duration, short time measurements (12 and 4 hours) were also made to study the diurnal variability and trends in the nitrogen compounds.

Cloud water measurements: Cloud water samples were collected on an hourly basis using an ASRC passive cloud collector (Kadlaeck et al., 1983). The collected samples were analyzed for pH immediately upon collection at the site. The samples were later analyzed for pH, conductivity, major anions and cations. Liquid water content measurements based on gravimetric technique (Valente, 1988) were also made simultaneously during cloud collection.

RESULTS

Ambient nitrogen pollutant concentrations: The observed nitric acid concentrations during the 1988 monitoring season ranged from 0.13-5.62 $\mu\text{g}/\text{m}^3$ and the mean concentration was 1.07 $\mu\text{g}/\text{m}^3$. The mean concentration of nitric acid for 1989 sampling season was 1.39 $\mu\text{g}/\text{m}^3$ while the range of values observed was between 0.55-2.60 $\mu\text{g}/\text{m}^3$. The concentrations of nitric acid observed at the Mt. Mitchell site are comparable to the measurements at other remote sites (Cadle et al., 1985; Shaw et al., 1982; Harrison and Allen, 1990). The gaseous ammonia varied from 0.01-4.98 $\mu\text{g}/\text{m}^3$ for 1988, and 0.2-3.23 $\mu\text{g}/\text{m}^3$ for 1989, while the mean values were 0.54 $\mu\text{g}/\text{m}^3$ and 1.47 $\mu\text{g}/\text{m}^3$ respectively. Gaseous nitric acid concentrations were in general higher in 1989. A diurnal variation was noted in the concentrations of nitric acid from the short time interval denuder measurements. Eight measurements each of 4 hours of duration were made during one day. The observed concentrations were found to peak during the afternoon hours (1200-1600). The daytime concentrations were significantly higher than the nighttime levels (2.5 $\mu\text{g}/\text{m}^3$ compared to 1.3 $\mu\text{g}/\text{m}^3$ in 1989; and 1.21 compared to 0.8 $\mu\text{g}/\text{m}^3$ in 1988 respectively). The observations are consistent with the photochemical pathway for the production of nitric acid during the daytime.

The precision associated with the ADS measurements was observed to be good. Collocated sampling runs produced similar concentrations (1.27 & 1.16 $\mu\text{g}/\text{m}^3$ for HNO_3). The laboratory and field blanks suggested no source of contamination.

The average concentrations of nitrogen dioxide were 2.5 ppb and 4.0 ppb for the 1988 and 1989 sampling seasons respectively. The levels of nitric oxide (NO) were always very low (usually less than the detection limit of the instrument, which is 2 ppb). The concentrations of nitrogen di-oxide were also consistently higher in 1989 than the 1988 values.

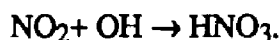
The mean concentrations of particulate ammonium were 1.4 $\mu\text{g}/\text{m}^3$ and 0.92 $\mu\text{g}/\text{m}^3$ for the 1988 and 1989 sampling periods respectively. Mean sulfate particulate concentrations were 4.35 $\mu\text{g}/\text{m}^3$ and 4.33 $\mu\text{g}/\text{m}^3$ for the 1988 and 1989 monitoring periods respectively. Nitrate concentrations (0.11 and 0.22 $\mu\text{g}/\text{m}^3$ for 1988 and 1989 respectively) were much lower compared to sulfate and ammonium. The aerosol fraction was thus dominated by sulfate particles followed by ammonium particulates.

Cloud Water Concentrations: The mean concentrations of nitrate in the cloud water samples were 195 $\mu\text{equ}/\text{l}$ in 1988, and 142 $\mu\text{equ}/\text{l}$ in 1989. The ammonium ion concentrations were 185 and 153 $\mu\text{equ}/\text{l}$ for the 1988 and 1989 field seasons respectively. The ionic concentrations in the cloud water were lower in 1989 compared to the previous years. Nitrate and ammonium contributed ~13% and ~15% respectively to the total ionic concentration in the cloud water.

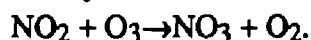
DISCUSSION

The concentrations of nitric acid measured during the course of one day in 1988 and 1989 were compared with the corresponding meteorological and ozone data to determine the generation and removal mechanisms for gaseous nitric acid. A multiple regression of HNO_3 concentrations on temperature, relative humidity, solar radiation and ozone of the 1988 data suggested that HNO_3 concentrations observed were related to the above variables with an r^2 of 0.9. Similar analysis for the 1989 data showed a good correlation of $r^2=0.97$. Solar radiation alone explained 75% of the variation in the nitric acid production in 1988 and ~50% variability in 1989. Relative humidity and temperature independently explained 74% and 65% of the variation in the nitric acid concentrations respectively for the 1988 measurements. A weak positive relationship between HNO_3 and ozone ($r^2 = 0.27$) was also observed.

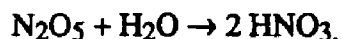
The correlation between the solar radiation and nitric acid suggests that the major pathway for the formation of nitric acid at Mt. Mitchell is oxidation of nitrogen di-oxide via OH radicals. Considerable levels of gaseous nitric acid were observed even during nights, though the concentrations reached a maximum during midday. The production of nitric acid during the daytime is believed to proceed through the reaction.



The oxidation of NO_2 by OH radicals does not occur during the night (no production of OH radicals). To account for the levels observed during night, an oxidation mechanism by O_3 may be present at Mt. Mitchell, since ozone levels are higher during the night than during the day at Mt. Mitchell.



NO_3 can combine with the existing NO_2 to produce N_2O_5 . Under high relative humidity conditions, N_2O_5 combines with water vapor in the atmosphere to generate nitric acid.



The Henry's law constant for gaseous nitric acid is 2×10^5 moles $\text{l}^{-1} \text{atm}^{-1}$ at 25°C (Schwartz et al., 1981). Using an average ambient concentration of 0.5 ppbv for gaseous nitric acid, the nitrate concentration in cloud water was analytically obtained to be ~ 130 $\mu\text{moles/liter}$. The measured average nitrate concentration in the cloud water samples were 195 $\mu\text{moles/l}$ and 141 $\mu\text{moles/l}$ during 1988 and 1989 which are higher than the Henry's law derived value. This seems to suggest that the incorporation of the pre-existing gaseous nitric acid/nitrate into the cloud accounts for most of measured nitrate concentrations in the cloud water. Though the pathways for the excess nitrate in the cloud water are not clear, oxidation of the dissolved nitrogen dioxide by dissolved hydrogen peroxide or ozone seems a possible mechanism at Mt. Mitchell. Sharp decreases in pH and ionic concentrations during the leading edge of an orographic cloud event may now be attributed primarily to initial droplet scavenging of gaseous nitric acid and deliquescence on pre-existing aerosol. Water vapor condensation and evaporation of the droplets have been suggested as important mechanisms in the leading and trailing edges respectively of an orographic cloud event. Thus, this role of HNO_3 may explain the concave trend (decreasing at the beginning and rising toward the end) observed in the concentration of the ions measured during an event (Kim & Aneja, 1990).

The heterogeneous removal of HNO_3 appears to have three possibilities:

1. the incorporation of nitric acid on to aerosols
2. the incorporation of nitric acid into precipitation/cloud droplets
3. dry deposition of nitric acid on surfaces.

According to our data, the incorporation of nitric acid on to aerosols does not seem to be present because of the following observations: (a) The concentrations of gaseous nitric acid were larger than the particulate nitrate levels by an order of magnitude; (b) The correlation between particulate nitrate and gaseous nitric acid were very low; (c) A diurnal variation, similar to that for gaseous HNO_3 was not observed for nitrate particulates. A rapid removal of nitrate particles must be occurring if the conversion of HNO_3 to nitrate particulates was indeed present. Such a short lifetime of an aerosol species seems unreasonable, because the deposition velocities are very small compared to the deposition velocity of the gas (1×10^{-3} cm/s for particles compared to 2.5 cm/s for gaseous nitric acid), and the scavenging of nitrate particles in the cloud/precipitation should be less than that for gaseous HNO_3 scavenging under similar conditions. Having a high deposition velocity (2-4 cm/s), dry deposition of nitric acid at the surfaces seems to be a likely removal mechanism in the absence of cloud/precipitation pathway.

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Disclaimer

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PARAMETERIZATION OF IN-CLOUD SCAVENGING OF SULFATES AND NITRATES IN ACIDIC DEPOSITION MODELS

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ABSTRACT

Scavenging of sulfates and nitrates -- two most common ions leading the cloudwater acidity -- was investigated during field studies atop a site in Mt. Mitchell (35°44'05"N, 82°17'15"W) State Park where the highest peak (2,038 m MSL) of the eastern U.S. is located. Experiments were conducted during the growing seasons (May 15 - September 30) of 1986 and 1987 using an instrumented meteorological tower (16.5 m tall) and a passive cloudwater collector. Clouds were frequently observed in which the Fraser fir and red spruce stands stayed immersed 28 % and 41% of the time during the 1986 and 1987 seasons respectively. Rate of cloudwater deposition on the forest canopy was determined using an inferential cloud deposition model. It was found by analyzing 9 short duration (lasting 8 h or less) and 16 long duration cloud events that the ionic concentration (SO_4^{2-} and NO_3^-) is inversely proportional to the rate (I_c) of cloudwater deposition (in mm h^{-1}) and can be expressed by the following relationship: $[\text{SO}_4^{2-}] = a I_c^{-b}$ or $[\text{NO}_3^-] = a I_c^{-b}$. The b values for predicting SO_4^{2-} concentration were found in the range of 0.14 - 1.24 for short duration and 0.062 - 0.63 for long duration cloud events respectively. The corresponding b values for predicting NO_3^- concentrations were 0.19 - 1.16 and 0.072 - 0.59 respectively. When b parameter was between 0.2 - 0.6, the correlation coefficients between measured and predicted ionic concentrations were found to exceed 0.7. The ratio of a parameter for SO_4^{2-} to NO_3^- varied between 1.75 - 6.95 indicating that the SO_4^{2-} contributes to the total ionic concentration substantially more than the NO_3^- . The above parameterization is similar to the one that is frequently used to relate ionic concentration in precipitation to the rainfall rate. Assuming that the SO_4^{2-} in cloudwater is the result of in-cloud scavenging of SO_4^{2-} aerosols in the cloud forming air mass, a functional dependence on the cloudbase temperature (T_{cb}) was found: $[\text{SO}_4^{2-}] = C \exp[T_{cb}/273]$ where C is a constant. Existing data from Piseco Lake (NY), Kilauea (HI), South Pole and McMurdo (Antarctica) have already shown conformity to the above relationship.

1. INTRODUCTION

Upon formation, clouds are very efficient scavengers of air pollutants if they lead to precipitation subsequently, while upon dissipation, in the absence of precipitation, they efficiently transform and redistribute the air pollutants in the planetary boundary layer. With regard to the interaction between pollutants and clouds, Scott¹ developed a mathematical model for which the SO_4^{2-} concentration in precipitation is predicted to be directly proportional to the SO_4^{2-} concentration of air ingested into cloud and inversely proportional to the liquid water content of cloud. Based on Scott's hypothesis, Hogan² interpreted the precipitated concentration of SO_4^{2-} ion as a function of cloudbase temperature with a natural logarithmic relationship. Furthermore, de Pena *et al.*³ investigated 10 precipitation events and showed the dependency of $[\text{SO}_4^{2-}]$ upon the precipitation intensity.

A study of cloud chemistry at Mt. Mitchell (35°44'05"N, 82°17'15"W; 2,038 m MSL), North Carolina, began in May, 1986. The current investigation are primarily focused on characterizing the chemical features of mountain clouds⁴ and assessing the relative contribution to acidic deposition through wet, dry and direct cloud capture mechanisms⁵. Based on the database obtained in 1986 and 1987, we present in this paper the representative cases of 9 short (lasting < 8 h) and 16 long duration cloud episodes by analyzing the micrometeorology, cloudwater chemistry and deposition flux over the cloud evolution period. Further, we present a scheme of parameterization of in-cloud scavenging of SO_4^{2-} and NO_3^- , based on the earlier studies^{1,2,3} and an evidence for relating the SO_4^{2-} concentration in precipitation (direct or occult) to the cloudbase temperature is investigated.

2. EXPERIMENTAL

At the Mt. Mitchell site, a 16.5 m tall tower was fully instrumented with meteorological sensors. The cloud water was hourly collected during the cloud episodes with an ASRC (designed by Atmospheric Science Research Center, State University of New York at Albany) collector placed atop the tower. The cloud episode was signaled when a stationary object at a distance of 1 km from the observation point became obscured by clouds and stayed consistently off the view for more than 15 min. The meteorological and micrometeorological parameters were measured. All the details of the experimental setup have been given elsewhere⁵.

The field observations began each year in May and ended in the middle of October, thus covering the duration of the growing season at the site. The observed cloud episodes are categorized into two classes: long ones exceeding 8 h, and short ones with duration less than 8 h. The former are found generally attributed to meso-scale or synoptic-scale disturbances and the latter are primarily the result of orographic lifting mechanisms. The cloud immersion was found^{4,5} to be 28% and 41% for 1986 and 1987 field seasons, respectively.

During the individual cloud episode, the rates of cloud water deposition were calculated for each hour with an inferential cloud deposition model which was first proposed by Lovett⁶ and further modified by Mueller and Weatherford⁷. This model is able to simulate the uptake of cloud water by the tree components (boles, branches and needles) within the forest canopy.

3. A PROPOSED METHOD FOR PREDICTING CONCENTRATIONS OF PRINCIPAL ANIONS: PARAMETERIZATION SCHEME FOR ACIDIC DEPOSITION MODELS

The SO_4^{2-} concentration in precipitation is a consequence of several cumulative processes occurring within and below clouds. Nucleation scavenging, Brownian motion, phoretic attachment, and inertial impaction primarily play a role in removing the SO_4^{2-} aerosols from air and attach them to the cloud and precipitation elements. In addition, SO_4^{2-} may be generated within the cloud and precipitation water through the oxidation of gaseous SO_2 . Scott¹ developed a mathematical model for calculation of SO_4^{2-} aerosol removal by precipitation. Scott¹ developed a mathematical model for calculation of SO_4^{2-} aerosol removal

by precipitation. The SO_4^{2-} concentration in precipitation is predicted to be directly proportional to the SO_4^{2-} concentration of air ingested into cloud and inversely proportional to the cloud water concentration. The airborne SO_4^{2-} scavenged by precipitation is strongly dependent upon precipitation formation mechanism in a certain portion of clouds. This can be mathematically expressed¹ as

$$f = \frac{14\,000 M_s(0)}{S_0 R^{0.88}} + \frac{750(1 - 4.41 \times 10^{-2} R^{-0.88})}{(1.56 + 0.44 \ln R)} \quad (1)$$

where f is a washout rate defined as the ratio of the SO_4^{2-} concentration in precipitation to that in air, S_0 is the SO_4^{2-} concentration of air just below the cloud base, $M_s(0)$ is the total SO_4^{2-} concentration of air contained in all hydrometers falling past a fixed level at the top of the riming zone, and R is the precipitation intensity. The model assumes that the in-cloud oxidation of SO_2 is negligible and the SO_4^{2-} deposited upon the ground represents the scavenging of pre-existing aerosols during the lifetimes of individual cloud elements.

Based on the Scott's hypothesis, Hogan² derived a formula to relate the SO_4^{2-} concentration in precipitation with the cloudbase temperature as expressed by

$$[\text{SO}_4^{2-}] = C \exp \left\{ \frac{T_{cb}}{273} \right\} \quad (2)$$

where T_{cb} is cloudbase temperature and C is a constant. He used this formula to correlate the earlier observations obtained in different cloud types (warm or cold clouds) and in different locations (Piseco Lake, New York State; South Pole, Antarctica; Kilauea, Hawaii), as shown in Fig. 1 with the dash-boxes. The SO_4^{2-} concentrations were found to be reasonably predictable by the cloudbase temperatures. Here, we use our database and the observations of Saxena *et al.*⁸ at McMurdo, Antarctica, which are listed in Table 1 to fit Eq. (2). The former were based on the ground measurements and the latter were obtained during airborne investigations. The results are shown in Fig. 1 with the solid-boxes. The temperature ranges of the data of McMurdo and Mt. Mitchell are similar to those of Piseco and Kilauea, respectively. The minimum values are found to be in good agreement with Hogan's prediction, but the averages for the results of both McMurdo and Mt. Mitchell are about three times that of Hogan's prediction. As shown in Fig. 1, the slope of our predicted semi-logarithmic line is approximately equal to that of Hogan's predicted line. The above method could be used to parameterize acidic deposition models and deserves further careful investigation under varying conditions of cloud forming airmasses, especially for the warm clouds such as the ones observed at Mt. Mitchell.

Eq. (1) for predicting the SO_4^{2-} concentration in precipitation can be further simplified as

$$[\text{SO}_4^{2-}] = a I_p^{-b} \quad (3)$$

where I_p represents the precipitation intensity (same as R) in mm h^{-1} which can be directly obtained from the precipitation collectors, and a and b are constants highly dependent on the cloud type³. Nitrate can be predicted with the same expression as Eq. (3) as well. It was found by de Pena *et al.*³ that b ranged from 0.34 to 1.71 (mean=0.47) and from 0.03 to 1.19 (mean=0.68) for SO_4^{2-} and NO_3^- , respectively, for 10 precipitation events.

We found that the cloud droplet capture mechanism essentially behaves somewhat similar to the precipitation scavenging. Thus, Eq. (3) can be implemented to predict the SO_4^{2-} concentration in cloud water by replacing the precipitation intensity with the rate of cloud water deposition (I_c) as has been computed for each cloud event with the cloud deposition model^{6,7}. Eq. (3) then becomes

$$[\text{SO}_4^{2-}] = a I_c^{-b} , \quad (4)$$

where I_c is the rate of cloud water deposition.

Selecting 9 short and 16 long cloud events with complete measurements for related parameters to fit Eq. (4), the results are listed in Table 2 in which r is the correlation coefficient between the measured and predicted SO_4^{2-} concentrations. Nitrate is also predicted with the same equation. The results show excellent correlation for most short cloud events with r greater than 0.75, but somewhat inconsistent in some cases with very low r for long cloud events. The b values for predicting SO_4^{2-} are in the range of 0.14 - 1.24 and 0.062 - 0.63 for short and long cloud events, respectively, whereas for NO_3^- , these are 0.19 - 1.16 and 0.072 - 0.59. When b falls between 0.2 - 0.6, the correlation coefficients between measured and predicted concentrations are mostly above 0.7 level. The average of b is well compared with the value of 0.3 suggested by Scott¹ and de Pena *et al.*³.

4. CONCLUSIONS

By analyzing 25 cloud events, our results support the previous findings for estimating SO_4^{2-} concentration in precipitation with the knowledge of related meteorological parameters. According to Scott's¹ hypothesis and Hogan's² inferred relationship, SO_4^{2-} concentration in the cloud water samples can be related to the average cloudbase temperature with a natural logarithm relationship, but our results are higher by a factor of 3 when compared to the Hogan's predictions. Scott¹ proposed a scheme for the parameterization of in-cloud scavenging of the SO_4^{2-} aerosol for which the concentration can be related to $R^{-\alpha}$, where R is the precipitation intensity in mm h^{-1} (similar to I_c) and α is a constant dependent on cloud types and the precipitation formation mechanism, and is suggested to be 0.3. Sulfate and NO_3^- concentrations in cloud water were found to be predictable by the inverse relation with the rate of cloud water deposition (I_c) calculated from the cloud deposition model during individual cloud episodes. According to our database, the predicted SO_4^{2-} and NO_3^- ion concentrations were in good agreement with the measured values having correlation coefficients above 0.7, when α ranged from 0.2 to 0.6. These findings will find usefulness in parameterization schemes of acidic deposition models.

ACKNOWLEDGMENTS

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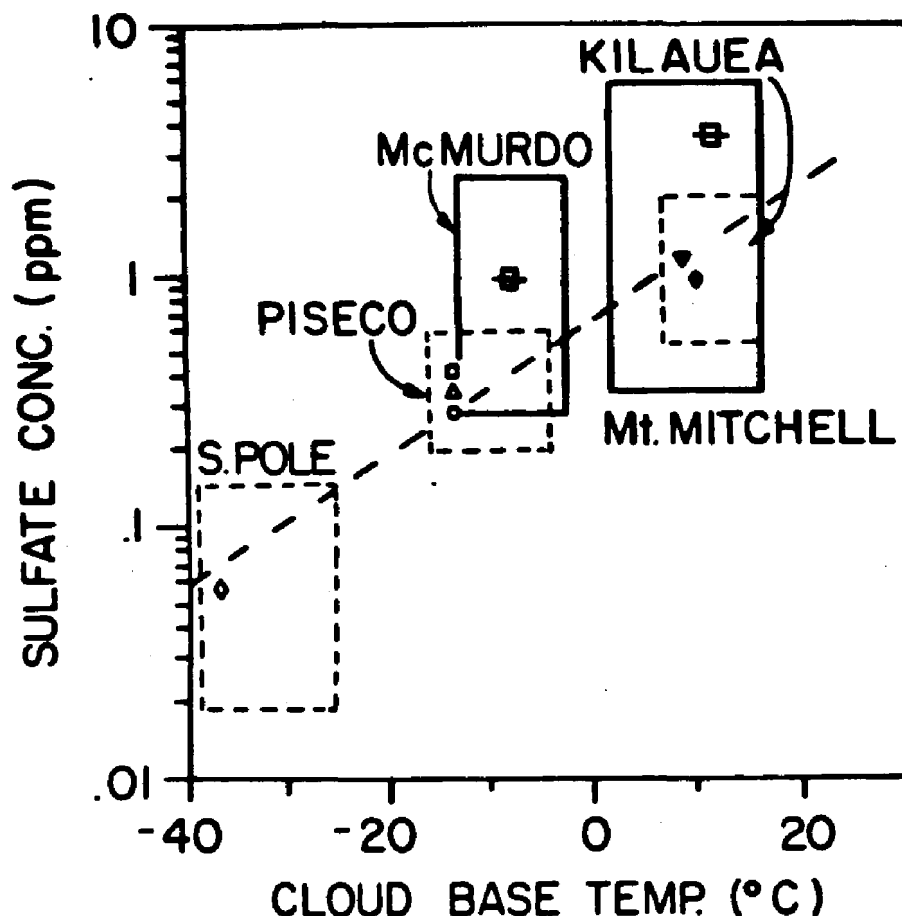


Figure 1. The sulfate concentrations as a function of cloud-base temperature. The ranges of cloud-base temperature and sulfate concentration are enclosed by labelled box. The solid-boxes are based on the data of Mt. Mitchell and McMurdo. The dash-boxes are duplicated from the figure of Hogan (1982). The mean values for the former are the squares with the horizontal bars and for the latter are open diamond, square, triangle and circle. For dash-box, the solid inverted triangles represent the values obtained in a single warm midaltitude storm and the open circle, triangle and square represent the values measured in a winter snowstorm with a similar wind structure.

Table 1 Sulfate chemistry of cloud water sampled at Mt. Mitchell, NC, and McMurdo, Antarctica.

Samples			[SO ₄ ²⁻] ^a (μeq l ⁻¹)	LWC (g m ⁻³)	Temp. (°C)	SO ₄ ²⁻ ^b (ppm)
McMurdo	6	range	31 - 330	0.01 - 0.18	-14 - -5	0.28 - 2.97
		mean	116	0.1	-9.5	1.04
Mt. Mitchell	86 (20 cloud events)		39 - 790	0.05 - 0.51	1.3 - 14	0.35 - 7.11
			370	0.23	10.8	3.33

a. Sulfate ion concentration measured in cloud water samples.

b. Sulfate concentration in air, converted from sulfate ion concentration measured in cloud water samples.

Table 2 Sulfate and nitrate concentrations as a function of the rate of cloud water deposition. N is the number of cloudwater samples, *r* is the correlation coefficient between the observed and predicted values, and *I_c* is the cloud deposition rate estimated from the cloud deposition model.

			[SO ₄ ²⁻] = <i>a I_c</i> ^{-b}			[NO ₃] ⁻ = <i>a I_c</i> ^{-b}		
Event	Type	N	<i>a</i>	<i>b</i>	<i>r</i>	<i>a</i>	<i>b</i>	<i>r</i>
24/06/86	S	4	729.669	0.341	0.901	298.522	0.229	0.536
29/06/86	S	3	146.551	0.602	0.984	31.568	0.609	0.983
01/07/86	S	3	593.496	0.144	0.885	85.810	0.294	0.996
02/07/86	S	5	70.776	0.681	0.778	18.274	0.576	0.768
05/07/86	S	3	565.619	0.138	0.996	187.526	0.193	0.979
11/07/86	S	4	68.420	0.679	0.880	35.792	0.772	0.897
19/08/86	S	4	4.138	1.239	0.784	1.263	1.158	0.847
14/05/87	S	3	88.682	0.270	0.658	41.209	0.305	0.727
21/05/87	S	6	334.204	0.262	0.811	94.211	0.292	0.876
03/06/86	L	11	316.670	0.062	0.075	85.654	0.072	0.084
29/06/86	L	10	140.957	0.303	0.669	43.76	0.290	0.665
09/07/86	L	7	883.455	0.326	0.882	231.396	0.156	0.431
10/07/86	L	11	399.895	0.235	0.239	82.001	0.319	0.417
12/07/86	L	5	97.085	0.341	0.957	45.829	0.402	0.970
29/07/86	L	8	1010.19	0.094	0.586	226.421	0.163	0.723
12/08/86	L	17	14.251	0.567	0.716	8.153	0.590	0.882
13/08/86	L	7	39.856	0.134	0.178	16.395	0.194	0.316
09/09/86a	L	6	67.619	0.629	0.616	139.645	0.133	0.423
09/09/86b	L	9	282.171	0.193	0.499	55.585	0.308	0.737
10/09/86	L	18	135.871	0.065	0.130	23.540	0.314	0.563
11/09/86	L	7	41.047	0.400	0.396	19.719	0.299	0.269
22/05/87	L	8	164.602	0.306	0.851	61.412	0.236	0.873
04/06/87	L	8	371.376	0.219	0.808	72.812	0.501	0.929
18/06/87	L	7	236.422	0.240	0.478	85.577	0.202	0.424
12/10/87	L	12	49.307	0.173	0.386	26.223	0.111	0.202

S = Short cloud event (duration < 8 hours)

L = Long cloud event (duration > 8 hours)

**MEASUREMENTS OF ATMOSPHERIC
HYDROGEN PEROXIDE IN THE GAS-
PHASE AND IN CLOUDWATER AT MT.
MITCHELL STATE PARK, N.C.**

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Abstract

Measurements of atmospheric hydrogen peroxide in the gas phase and in cloudwater were made at the Mt. Mitchell State Park, North Carolina, during the growing season (May through September) of 1988. Cloudwater hydrogen peroxide was also measured during the late summer and fall of 1987 (August and October). Levels were found to be similar to those reported for another high elevation location in the southeastern United States. Cloudwater samples collected during these periods showed a wide range of levels (~ 0 to 219 $\mu\text{moles/liter}$) and average values of 38 $\mu\text{moles/liter}$ and 44 $\mu\text{moles/liter}$ for the entire sampling sessions of 1988 and 1987, respectively. Significant seasonal variation was noted both in 1987 and 1988, with cloudwater levels of hydrogen peroxide much higher in the summer than in the fall.

Gas-phase hydrogen peroxide levels ranged from nearly zero to above 3 ppbv. Gas-phase hydrogen peroxide demonstrated a nighttime maximum in the summer but not in the fall. This reverse diurnal pattern is unlike the typical pattern of a daytime maximum, as observed in most locations.

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Introduction

Ambient hydrogen peroxide plays an important role in the aqueous phase chemistry of precipitation acidification, and may be the primary oxidant involved in the production of aqueous phase sulfuric acid in cloudwater, when the pH is less than 4.5^(1,2). Like ozone, hydrogen peroxide is a strong oxidizing agent. At least one study, conducted on Norway spruce, indicated that hydrogen peroxide-containing mist can cause damage to trees⁽³⁾. Since hydrogen peroxide is formed from the recombination of peroxy radicals when atmospheric levels of NO_x are low enough such that NO does not compete for consumption of HO₂•, this may be significant to the rural eastern United States, where acid deposition and air pollution have been thought to be the cause of, or at least contribute to, the forest decline in the Appalachians. For these reasons gas phase and cloudwater levels of hydrogen peroxide were measured, in conjunction with other chemical, physical, and meteorological parameters, during the growing seasons of 1987 and 1988 at Mt. Gibbs, a mountain adjacent to Mt. Mitchell in western North Carolina and where significant forest decline is reported⁽⁴⁾.

Experimental

Ambient, gas-phase hydrogen peroxide was measured using the continuous fluorometric analyzer based on the horseradish peroxidase method⁽⁵⁾ periodically during the latter portion of the growing season (July through September) of 1988 at the high elevation site (Site 1) at Mt. Gibbs, N.C. The dual channel fluorometric analyzer measures total peroxides on one channel, and by specific enzymatic destruction of hydrogen peroxide, organic peroxides only on the second channel. Hydrogen peroxide is obtained by difference. Gas phase total and organic peroxide data were recorded on a chart recorder and extracted manually as 12-minute averages. These data were then consolidated into hourly averages. The hydrogen peroxide analyzer was calibrated at least once daily, and calibration solutions were checked weekly. Baseline checks were performed automatically, usually several times per day.

Cloudwater samples were collected hourly at both sites 1 and 2, "fixed" for hydrogen peroxide according to the derivatization technique⁽⁶⁾ to minimize losses due to decomposition, and immediately refrigerated. These samples were later sent to the Tennessee Valley Authority lab in Muscle Shoals, Alabama, where they were analyzed by the fluorometric technique adapted for precipitation samples⁽⁷⁾ for hydrogen peroxide content. A limited number of samples were collected in 1987, during August and October. A larger data set was collected in 1988.

The Mt. Gibbs research station, the meteorological and climatological parameters measured there, and the quality assurance protocols, have been described previously^(7,8). Unless otherwise noted, statistical significance is assumed to be at the 99 % confidence level.

Results and Discussion

Gas-phase Hydrogen Peroxide

During the field season of 1988, 273 hourly hydrogen peroxide measurements were recorded. Gas-phase hydrogen peroxide at Mt. Mitchell ranged from ~0 to 3.3 ppbv. In general, atmospheric hydrogen peroxide levels at the Mt. Mitchell State Park are comparable, or higher than, values reported in the literature. At nearby Whitetop Mtn, VA⁽⁹⁾, a maximum of 2.6 ppbv was reported in the summer of 1986, and a maximum of 0.57 ppbv in the fall. Values over 4 ppbv have been observed aloft, over the eastern United States⁽¹⁰⁾.

Statistically significant seasonal variation in the ambient hydrogen peroxide level during 1988 was observed, with summertime levels of hydrogen peroxide (mean 0.62 ppbv) significantly greater than those observed in the fall (mean 0.19 ppbv). Other researchers have noted similar seasonal variations in ambient hydrogen peroxide. A strong seasonal dependency was also observed at Whitetop Mountain⁽⁹⁾ with highest levels in both the gas and liquid phases occurring during the summer, and lowest values in the spring and fall. In 1988, a seasonal variation was noted in the ambient ozone levels as well, with summertime levels were higher than fall levels at Mt. Mitchell⁽¹¹⁾.

Nighttime hydrogen peroxide levels measured during the summer of 1988 (mean 0.77 ppbv) were significantly higher than daytime levels (mean 0.46 ppbv). This result was not expected, based on our current understanding of the photochemistry of hydrogen peroxide formation. Atmospheric hydrogen peroxide is formed in the absence of NO from the combination of hydroperoxyl radicals, which are formed from the photooxidation reactions of reactive hydrocarbons or of carbon monoxide. The nighttime maximum in ambient hydrogen peroxide at Mt. Mitchell is very different from the typical diurnal pattern reported in the literature. In southern California⁽¹²⁾, a daytime maximum in hydrogen peroxide was observed in the early afternoon, corresponding to a minimum in the NO_x and a maximum in the O₃, 1 to 3 hours after the daily peak of solar radiation. Daytime values exceeded the nighttime values by 26% at Whitetop Mountain, VA⁽⁹⁾. The reversed diurnal trend observed at Mt. Mitchell was not noted during the fall, where the nighttime levels (mean 0.20 ppbv) were not found to be significantly higher than the daytime levels (mean 0.17 ppbv).

The reason for the nighttime maximum in ambient hydrogen peroxide at Mt. Mitchell is still unknown, but because of the elevation of Site 1 (2006 m MSL), it is possible that, during the night, the mountaintop is above the nocturnal boundary layer, which might allow the mountaintop to be exposed to the free tropospheric, H₂O₂-rich air above the mixed layer; a vertical gradient in ambient hydrogen peroxide, increasing with height, has been reported⁽¹⁰⁾. Within the mixed layer itself, losses of ambient hydrogen peroxide would be high due to deposition to the forest and decomposition on dirt or water surfaces. Above the mixed layer, these losses would be minimized.

Cloudwater Hydrogen Peroxide

Cloudwater hydrogen peroxide levels at Site 1 ranged from 0 to 219 μM during 1988. The mean hydrogen peroxide level was 38 μM at Site 1 and 49 μM at Site 2 (however, this difference was not statistically significant at the 95 % level). Cloudwater levels at Mt. Mitchell have also been found to be comparable or higher than most cloudwater levels reported elsewhere. The only higher values reported in the literature were for Whitetop Mountain, VA⁽⁹⁾, where a maximum of 247 μM was observed in the summer.

Fall hydrogen peroxide levels were much smaller at Mt. Mitchell (maximum 55 μM). In this work, seasons are roughly defined (at Site 1) as May and June being spring, July and August being summer, and September being fall. Based on this definition of the seasons, the levels for spring, 1988, (mean 57 μM) were not significantly higher than those of summer (mean 47 μM). However, the summer concentration was significantly higher than that of fall (mean 17 μM) (99 % confidence).

Cloudwater samples were analyzed according to whether the cloud event was "long" (8 hours or longer) or "short" (less than 8 hours)⁽⁷⁾. This classification was intended to give an indication of the type of cloud; short cloud events are usually orographic in nature, while the long events generally tend to be frontal in origin. Based on this categorization, short events have been reported to exhibit significantly higher concentrations of all ionic species and lower liquid water content than long events exhibit^(7,8). The ratio of concentration in the long event cloudwater to the concentration in the short event cloudwater was 0.52, 0.52, 0.50, and 0.58 for SO_4^{2-} , NO_3^- , NH_4^+ , and H^+ , respectively. The ratio of liquid water content for the short event to the long event was 1.8 (the inverse of which is 0.56). Therefore, dilution may be responsible for the difference in ionic concentrations between long and short events. In contrast, although the hydrogen peroxide content of the short event is significantly higher than that of the long event (95% confidence), the ratio of the concentration in long events compared to short events is 0.71, which is significantly higher than the ratio for other cloudwater species, indicating that, although there seems to be an inverse relationship between cloud liquid water content and hydrogen peroxide content, dilution is not the only factor determining the cloudwater content of hydrogen peroxide. This inverse relationship may be more a result from equilibration processes rather than dilution processes.

The cloudwater hydrogen peroxide content was compared to that predicted by the Henry's Law constant for those periods in which there were simultaneous measurements of cloudwater and gas phase H_2O_2 and temperature. The Henry's law constant is given by⁽¹³⁾:

$$H = \exp\left(\frac{A}{T} - B\right) \quad (1)$$

where H, the Henry's law constant, has units of M atm^{-1} , T is in degrees Kelvin, $A = 6621$, and $B = 11$.

Good agreement was found between the liquid and gas phase concentrations of hydrogen peroxide, with the slope of the line = 0.8, and the correlation coefficient $r^2 = 0.84$. Usually, the aqueous phase concentration has not quite reached equilibrium with the gas phase level. Exceptions occur mostly at very low concentration (gas phase hydrogen peroxide less than about 0.2 ppbv), which may be due to the approaching of the level of detection for the ambient air instrument.

Conclusions

Hydrogen peroxide levels at Mt. Mitchell were comparable, or higher, than those levels previously reported in the literature. Gas phase hydrogen peroxide levels reported previously in the literature for other sites which were higher than Mt. Mitchell levels were found aloft. Cloudwater levels at Whitetop Mtn, VA, were the only cloudwater levels found to be higher than those at Mt. Mitchell. Due to the southern location of the Mt. Mitchell site and the observation of the latitudinal gradient of hydrogen peroxide, with levels increasing as we move south, this is consistent with other observations reported in the literature.

Contrary to the typical diurnal variation observed at most monitoring sites, with midday maxima, gas phase hydrogen peroxide at Mt. Mitchell exhibits a significant "reverse diurnal variation", in the summer, but not necessarily in the fall. This may be explained by the lowering of the nocturnal boundary layer to below the mountaintop at night, so that the site is exposed to free tropospheric air, which could contain higher levels of hydrogen peroxide. A vertical gradient of hydrogen peroxide, increasing with increasing elevation, has previously been reported in the literature.

Consistent with our current knowledge of the behavior of hydrogen peroxide at other locations, there is significant seasonal variation in the gas phase hydrogen peroxide concentration at Mt. Mitchell, with levels dropping in the late summer and fall.

Cloudwater hydrogen peroxide content depends on chemical parameters and cannot be explained on the basis of dilution alone, like the ionic species. It does, however, appear that the liquid water content of the cloud does have an effect on the level of hydrogen peroxide in the cloudwater, although this effect is not as significant as the effect on ionic species.

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MODELING OROGRAPHIC CLOUD WATER DEPOSITION AT MT. MITCHELL, NC: THE EFFECT OF LOCAL TOPOGRAPHY

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A two-dimensional orographic cloud model MCCC PLUVIUS is applied to the Mt. Mitchell Mountain Cloud Chemistry Project (MCCP) site in order to examine possible sources of variability within sampling site measurements due to topographic forcing. Model simulations are used to determine the effect of local topography on observed pollutant deposition and cloud water concentrations. The dissolved pollutant concentration at the mountain summit was found to be highly dependent on the distance over which deposition occurred. The equilibrium balance between pollutant loss through deposition and replacement by turbulent diffusion is shown to vary with cloud size. Orographic clouds generated by trajectories crossing the summit from west to east are found to produce more acidic clouds at the Mt. Mitchell MCCP site for small to moderate sized clouds, while the clouds passing from east to west are more acidic for exceptionally moist flows. The use of sampling site measurements to classify atmospheric conditions is shown to be inconclusive.

Introduction

The summer of 1988 was among the driest ever recorded for the southeast. Despite these conditions, Mt. Mitchell, NC (elev 2037 m) was within a cloud 960 hours out of a total of 3260 hours sampled, representing 29% of the total time. The extreme presence of clouds present at this elevation, even during a period of regional drought, as well as their ability to scavenge available pollutants from the atmosphere has lead to the hypothesis that clouds are one of the leading mechanisms for the transfer of atmospheric pollutants to the above cloud base forests. The Mountain Cloud Chemistry Project (MCCP) was initiated in order to investigate the role of direct cloud water interception as a mechanism in the decline of the high altitude forests of the Appalachians¹. As part of the project, a two-dimensional orographic cloud model MCCP PLUVIUS was developed to aid in the evaluation of the data collected at field sites². PLUVIUS simulates the chemical and physical processes associated with orographic cloud formation as a result of air flow over a mountain, including aerosol and gaseous scavenging, in-cloud chemical transformations, and cloud water deposition.

In 1988, over two-thirds of the time that clouds were present at the summit sampling site at Mt. Mitchell (Site 1), the local wind direction was observed to be within 20° of the normal to the ridge axis. Observations show that this is the result of channeling the wind field between adjacent ridge lines. Thus it is possible for similar wind conditions at Site 1 to result from radically different trajectories. In general, the easterly facing slope of the Mt. Mitchell is steeper than the westerly facing slope, and the prevailing wind crosses the ridgeline from west to east approximately 60% of the time. In order to evaluate the performance of PLUVIUS based on measurements made at Mt. Mitchell, we must therefore first be able to assess the influence that local topography will have on the resultant model prediction.

Evaluation of Topographic Influences

The local topography used within PLUVIUS determines the relative distance from the sampling site at which a cloud will form along a streamline, and consequently, how far the cloud must travel until reaching the site. Two parameters that effect the dissolved pollutant concentration and cloud water deposition within the model are turbulent diffusion and deposition through impaction. Turbulent diffusion within the model continuously acts to redistribute areas of high and low concentrations of a quantity in order to produce a more uniform distribution. Deposition within the model, on the other hand, only takes place when a the column of air being advected over the mountain becomes saturated in the layer adjacent to the forest canopy.

Deposition within PLUVIUS is parameterized by a relationship provided by Lovett³ which is assumed applicable to the Mt. Mitchell forest. Since Deposition through impaction is generally much larger than that for settling given the typical wind speeds found in a mountain cap cloud, deposition through settling is neglected. Turbulent diffusivity is based upon mixing length considerations using a value of $10 \text{ m}^2 \text{ cm}^{-1}$ suggested by Luecken *et al.*¹ for a moderately stable environment.

The effect of local topography on the above parameterizations was tested using a base case chemical atmosphere, and three soundings each representing different magnitudes of orographic cloud formation. Various topographic profiles were implemented to explore the general effects of trajectory slope on cloud development and deposition. The initial height of a streamline was constant for each profile tested, as was the summit height. Topographic profiles derived from the terrain surrounding Mt. Mitchell were then used as input to the model to examine the effect which local topography may have on measurements obtained from the Mt. Mitchell MCCP site.

Results and Discussion

Pollutant concentrations at the cloud base were found to drop quickly once deposition was initiated (Figure 1). This condition is the result of the relative inefficiency of diffusion to replace pollutants lost through deposition when the mass flux is large. After the initial drop, the pollutant concentration reaches a point at which the mass flux out of the cloud approaches an equilibrium with diffusion of pollutants from the surrounding air into the cloud base producing a much more gradual decline. From Figure 1, the pollutant value sampled at a sampling site can be seen to be a function of the distance over which deposition occurred. Trajectories that rise steeply once saturation is reached in the column base travel a shorter horizontal distance above cloud base, thereby reducing the distance over which deposition occurs; thus, higher spatial pollutant concentrations result.

Pollutant mass lost through deposition within the model is replaced only through diffusion; alternatively, liquid water lost through deposition is replaced not only by diffusion, but by additional condensation if lifting continues. Therefore the pollutant mass within a cloud is affected to a higher degree by deposition than is the liquid water content (LWC). In opposition to deposition which is only invoked once a cloud forms, diffusion is always acting to redistribute areas of high and low concentration. In this manner, diffusion acts to dissipate saturation within the cloud over the entire length of the trajectory. Steeply sloped trajectories resulted in higher LWC's than did those with more gradual slopes. This result lead to lower dissolved pollutant concentrations for steep trajectories. As a result, steep trajectories which favored higher pollutant masses through less deposition were often coincident with conditions favorable for greater dilution of the pollutants remaining in the cloud.

When local topography was introduced into the model, small to moderate clouds ($\leq 0.6 \text{ g m}^{-3}$) resulting from trajectories passing over the Mt. Mitchell ridge from west to east were found to be more acidic than those originating from the east. This is in general agreement with experimental results reported by Saxena *et al.*⁴ The amount of variability decreased with increased cloud size, ranging from 3.0 - 3.5 pH for an LWC of 0.1 g m^{-3} to 4.6 - 4.8 pH for an LWC of 0.6 g m^{-3} . In the case of small clouds, the distance over which deposition occurred is very small in comparison to the distance over which diffusion occurs. In these cases, the steeper trajectory (originating from the east) produced the greatest LWC, and therefore the greatest pollutant dilution. For very moist clouds ($> 0.6 \text{ g m}^{-3}$) in which deposition occurred over a long distance, clouds passing from east to west were found to be more acidic. For this case, the distance over which deposition occurs becomes of an order comparable to that of diffusion. Depletion of pollutants thus limits the acidity of clouds when diffusion cannot balance the mass flux out of the column, and since steeper trajectories decrease the distance over which deposition occurs, these trajectories may produce more acidic clouds.

Conclusions

Local topography was found to greatly influence the pollutant concentration within the model cloud and the pollutant deposition to the mountain. When actual topography was introduced, trajectories approaching Site 1 from the west side of the ridgeline were found to generally produce more acidic clouds than those approaching from the east. In large clouds where depletion of pollutants is important, the steep eastern facing side of the Mt. Mitchell ridge produced the most acidic clouds. The model parameterizations for deposition and diffusivity strongly influence the equilibrium concentration of pollutants within a cloud, and should be taken into account when comparing model predictions to observed conditions. Topographic forcing of the flow field is therefore an important contributor to the values measured at the Mt. Mitchell MCCP sites. Clouds resulting from similar air masses and observed wind conditions on the mountain can display significantly different characteristics in pollutant concentrations. Alternatively, similar cloud acidity does not necessarily imply a similar pollutant environment. It may therefore be misleading to classify an airmass or cloud environment based solely on field measurements.

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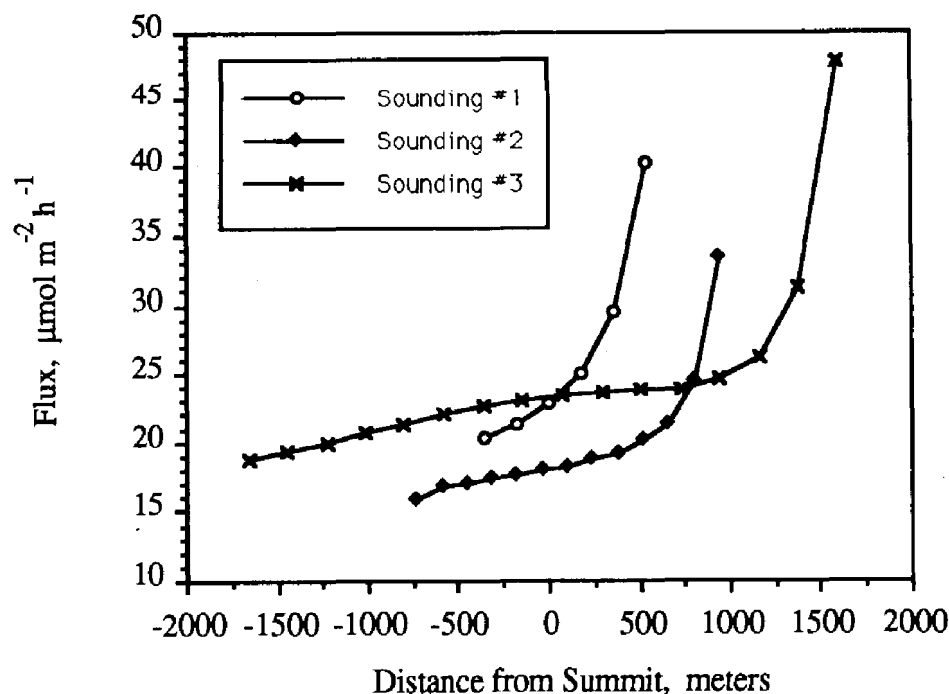


Figure 1. Hydrogen ion (shown as a representative field) flux to the model mountain surface for three sounding cases using a gaussian mountain. Positive X direction is upwind of the mountain.

**Remote Site Cloud Condensation Nuclei 'Fingerprints':
Indicators of air-mass transport and mixing**

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The cloud condensation nuclei, CCN, concentration was measured in Mt. Mitchell State Park, NC during the summer of 1988, in conjunction with the Mountain Cloud Chemistry Project, to help further the understanding of the physico-chemical characteristics of the air which delivers wet acidic deposition to forests. The CCN measurements in this study were made using a CCN-Spectrometer, and they ranged between <100 and $3,600 \text{ cm}^{-3}$. The synoptic conditions, the local meteorological and the microphysical parameters (i.e., total droplet concentration) were used to establish whether air-mass transport or mixing yielded the measured CCN concentrations. Large variations in CCN concentration ($\geq 200 \text{ cm}^{-3} \text{ h}^{-1}$) were found to be related to the sampling of a non-homogeneously mixed air parcel or near the boundary of different air-masses. Large temporal CCN variations that occur near the end of an event are likely due to evaporation. More subtle changes in the CCN concentration ($< 200 \text{ cm}^{-3} \text{ h}^{-1}$) were associated with air-mass transport.

1. Introduction

The cloud condensation nuclei, CCN, concentration was measured in Mt. Mitchell State Park, NC during the summer of 1988, in conjunction with the on going measurements of the Mountain Cloud Chemistry Project, to help further the understanding of the physico-chemical characteristics of the air delivering the wet acidic deposition to the local forests. Such measurements are the first in this area, although they have been made elsewhere¹⁻⁸. The relation of CCN measurements to their source^{5,8} (e.g. maritime, continental, evaporation), and to the dynamics⁹ involved in producing a critical supersaturation with respect to water vapor and hence the microstructure of clouds is known. The intent is to enhance the present knowledge by uniquely applying this data to the question of whether air-mass transport, or mixing, yielded the measured CCN concentrations. My measurements suggest the existence of a threshold magnitude of the time rate of change in the CCN concentration ($\geq 200 \text{ cm}^{-3} \text{ h}^{-1}$) that is associated with the non-homogeneous mixing of different air parcels or air-masses (e.g. near their boundaries, evaporation). Temporal changes in CCN concentration less than the threshold are associated with synoptic scale transport. Knowing how the CCN, in the air that flows across the site, are generated would be a beneficial input to acid deposition models since this knowledge would make such models more indicative of the present dynamical processes, the source and the physico-chemical characteristics of these aerosols. The accuracy and operationality of these models will also improve. CCN measurements would also prove valuable in investigations related to the effect that they might have on climate, e.g. dimethylsulfide and climate¹⁰, or even on cloud formation in other planetary atmospheres.

2. Background

Measurement of CCN

The instrument used to measure the CCN¹¹, termed the CCN-Spectrometer (Figure 1), yields a continuous measure of the number of aerosols activated over the entire range of atmospheric supersaturations in any instant. The ability of tackling the problems associated with the role of the physical-chemical characteristics of the aerosols on the formation of clouds was allowed, for the first time, on the order of the lifetime of a cloud. By 1988 a similar spectrometer³ had evolved. It consists of 5 to 8 basic thermal gradient diffusion chambers in series with a ROYCO particle counter capable of simultaneously counting five different particle size ranges at the exhaust end of the instrument from which a supersaturation profile is inferred. The CCN-Spectrometer produces a supersaturation profile, equivalent to that yielded by a number of basic thermal gradient diffusion chambers in parallel, which is derived from the variation of the vapor density profile across the width of the chamber due to the difference between the top and bottom plate temperature profiles across the width of the chamber. The desired supersaturation range is obtained by adjusting

the temperature difference between the two plates. The resulting activated particles are counted by a CLIMET 208 particle analyzer as its inlet sweeps the entire width of the chamber within fifteen seconds. See Fukuta and Saxena¹¹ for details.

Cloud condensation nuclei (CCN) spectra were measured before, during, and after each event. The data was fitted to the standard functional relationship between supersaturation, S , and cloud condensation nuclei, CCN, namely

$$N = C S^k, \quad (1)$$

where N is the number concentration of CCN per unit volume with critical supersaturation less than S (in percent); C is the concentration parameter of the distribution and k is its slope parameter. The CCN-Spectrometer measures N at any given range of S instantaneously. The value of k is related to the dynamics involved in producing the S ⁹. A k value very much less than one, i.e., <0.6 , implies the cloud droplet concentration is essentially determined by the composition of the CCN concentration active at different supersaturations. A k greater than unity suggests that the cloud droplet concentration is more related to the rate of the ascent, which is proportional to the rate of the supersaturation generation (dS/dt), rather than to the aerosol content. Such k values may also be the result of existing CCN source regions, since recently generated particles are likely to be small and require high activation supersaturations yielding higher k values¹².

Site Description

The site in the Mt. Mitchell State Park, NC is located on Mt. Gibbs (≈ 3.2 km southwest of Mt. Mitchell), which is located in the westernmost portion of the state, and consists of a 17.1 m walk up tower equipped with temperature, pressure, wind speed, wind direction, and humidity instruments near its top. A carriage, positioned on the tower's northern face, carries the Atmospheric Science Research Center (ASRC) passive teflon string cloudwater collector, and the Particle Measuring Systems Forward Scattering Spectrometer Probe (FSSP) from the ground to as high as a couple of meters above the top of the tower. An instrument shed at the base of the tower houses the gaseous instruments which are hooked into a sampling manifold that extends to the top of the tree canopy (approximately 12.1 m below the top of the tower). The CCN-Spectrometer was operated from a tool shed located about 8.0 m to the northeast of the tower. Its inlet is an inverted funnel (0.1 m diameter) that extends 0.5 m out from and whose opening is 2 m above the top of the shed. Further details of the site are given in Saxena et al.¹³.

3. Results and discussion

The CCN measurements at our site ranged between <100 and $3,600\text{ cm}^{-3}$ and are consistent with other studies². The $\leq 100\text{ cm}^{-3}$ CCN concentrations were also measured in the Olympic Mountains¹⁴ and have been observed to follow widespread rain⁸. CCN concentrations $\leq 200\text{ cm}^{-3}$ are typical of maritime air-masses^{5,15}. Unpolluted continental air-mass concentrations^{8,15} are usually between 200 and $\approx 2,000\text{ cm}^{-3}$, while polluted continental air-masses have concentrations above $2,000\text{ cm}^{-3}$. Table I shows the typical total CCN concentrations (based on $S=0.92\%$) and the respective k parameter for the given time periods before and after four cloud events during the 1988 field season. The events in this table are associated with air-masses that range from maritime (JULY 22) through 'aged' - continental (JUNE 30). Two of the events in Table I (namely, JUNE 30 and SEPTEMBER 24) are accompanied with no change in air-mass, while the remaining two events (namely, JUNE 24 and JULY 22) are. The values in this table are based on averages of 3 h or longer. The JUNE 24 and JUNE 30 events occurred under different meteorologically dynamic processes¹⁶. Observations suggest that the pre-JULY 22 CCN concentrations of $\leq 100\text{ cm}^{-3}$ are due to the 24 h a-priori period of widespread precipitation. It is possible that the low CCN measurements may be due to operational shortcomings of the instrument during this time. Regardless of the reason, a misinterpretation of the measurement is inevitable. The CCN measurement of $3,600\text{ cm}^{-3}$ was taken near the end of the JUNE 24 cloud event. If this measurement is encountered, after the fact by a modeler, it might be interpreted as a change to a polluted air-mass. This would imply that a different composition and source of the activated aerosol reached that site. For example, such a measurement could be due to evaporation in which case the sampled aerosols are likely to have the same general characteristics as those prior to the evaporation. An illustrative case, i.e., June 24-25, 1988, is presented.

Case Study

June 24-25, 1988. The June 24-25, 1988 event began at 1630 EST with thunderstorms that delayed sampling until 1926 EST and continued for another 9.5 h as a surface high, which extended itself into the Great Lakes, the mid-west and the mid-Atlantic states 12 h prior to this event (Figure 2a), became oriented southwest to northeast by 0700 EST June 25 due to an eastward moving southern Canadian frontal system (Figure 2b). The 850 mb level, the closest standard vertical level to our site ($\approx 810\text{ mb}$), shows a large high pressure system centered south southeast, SSE, of the site that extended north to off the South Carolina coast 12 h prior to this episode (Figure 3a). The high strengthened as its center moved northwestward, NW, and south of the site (Figure 3b) by 1900 EST June 24. A low moving eastward, E, across southern Canada strengthened the high pressure (now located over mid-southern Tennessee) by 0700 EST June 25 (Figure 3c). The winds at 850

mb went from moderate northwest, NW, 12 h prior to the event to light and variable at 1900 EST June 24 to moderate-strong west northwest, WNW, by 0700 EST June 25. Figure 3c also shows that the 850 mb 24-48 h back trajectories (ending 0700 June 24 (2) and 0700 EST June 25 (1)) shifted from WNW to NW flow during the course of this event. The 500 mb level, i.e., the level which steers synoptic systems, is typical for summer in this area, namely, placid. The shift in the windfield, particularly at 850 mb and at our site, corresponds to the passage of an upper level disturbance.

Figure 4a shows the temporal variation of the total droplet concentration, N_d , and the cloud condensation nuclei concentration, CCN. The N_d varied between 75 and 500 cm^{-3} while the CCN concentration ranged between 60 and 3570 cm^{-3} . A period of light drizzle was observed between 0103-0203 EST and explains the latter peak in the droplet concentration. The slightly earlier peak (i.e., 0003-0103 EST) corresponds to a bimodal cloud droplet spectra. The total droplet and CCN concentration values show a significant change after the 2 h period ending 0203 EST compared to before it, excluding the likelihood of evaporation during the last part of the event. This change is also evident in the concurrent variations of the cloudwater ions. The site wind direction is also given at the top of this figure. The wind direction begins to shift westward toward north around 0100 EST. The 0.3h averaged pressure dropped by 1.0 mb (P) between 0145 and 0200 EST. The segment of the CCN curve between the open boxes (0218-0309 EST) represents a time rate of change in the magnitude of the CCN concentration of $\geq 200 \text{ cm}^{-3} \text{ h}^{-1}$ ($208 \text{ cm}^{-3} \text{ h}^{-1}$). The open oval, in a similar vein to the open boxes, denotes the onset of evaporation. The 0.3 mb averaged pressure rose by 1.0 mb (circle P) between 0645 and 0700 EST. Figure 4b shows the primary ions, excluding H^+ , present in the collected cloudwater. The early event maximum, especially in the case of sulfate, may be the result of additional sulfate production caused by the scavenging of the 100 ppb ozone concentrations present at the beginning of this event¹⁷. The minimum in the concentration of these ions is likely due to the presence of precipitation, and the rebound could be indicative of a new source of CCN. Evaporation may also have enhanced this rebound. Note that all of the cloudwater ions had the same temporal pattern. The measured CCN spectra showed two, occasionally three, different C and k parameter sets to exist (for example, at 2118, 0437 and 0456 EST), and may be due to measuring polluted air. Saxena (1980) also attributed such to the sampling of non-steady state circumstances. While the nonconformity to Eq. 1 at 2118 EST may possibly be due to inhomogeneous mixing between maritime and continental air-masses^{2,15}, the latter two occasions (i.e., 0437 and 0456 EST) are due to the non-steady state occurrence of evaporation since they were measured at the end of this event. The change in the total droplet concentration, the CCN concentration, the local meteorology and in the ionic composition of the cloudwater is in phase with that from the synoptic scale meteorology (Figure 2-3).

4. Concluding remarks and recommendation

The real-time measurement of CCN spectra (i.e., CCN concentration versus supersaturation), or the CCN "fingerprint", was found to be indicative of air-mass transport and mixing. The use of these fingerprints in conjunction with microphysical, meteorological and chemical measurements could be quite beneficial in making acid deposition models more indicative of the present dynamical processes, the source and the physico-chemical characteristics of these aerosols. The consequential result would be an increase in the accuracy and in the operability of these models. Studies relating to the effect that CCN might have on climate change and those relating the role CCN might play in other planetary atmospheres would also benefit.

The results of the case studies are summarized;

- The magnitude of the temporal change in CCN concentrations of $<200 \text{ cm}^{-3} \text{ h}^{-1}$ are associated with the transport of an air-mass associated with a frontal system, an upper level disturbance, or the rising of local valley fog. However, in contrast, a $\geq 200 \text{ cm}^{-3}$ change in the magnitude of the CCN concentration, for example, from 100 cm^{-3} to 300 cm^{-3} , implies that sampling was first conducted in a maritime air-mass that switched to a clean continental air-mass. Such a change that is $<200 \text{ cm}^{-3}$ is not interpreted as a change in air-mass.
- The magnitude of the change in CCN concentrations of $>200 \text{ cm}^{-3} \text{ h}^{-1}$ is due to sampling near the boundary of a frontal system, upper level disturbance, two different air-masses, or within a non-homogeneously mixed air parcel. At the end of an event such a change in CCN concentration is most likely result from evaporation.

Further research using CCN measurements in conjunction with microphysical, chemical and meteorological processes is highly recommended.

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Table I Representative total CCN concentrations of measured CCN spectra (based on $S=0.92\%$) and the respective k parameters for the given time periods (parentheses) before and after the sampling of four cloud events in 1988. Also shown is the duration of the respective cloud events

EVENT	CCN CONCENTRATION (cm^{-3})		EVENT DURATION
	BEFORE	AFTER	
JUNE 24	344, $k=1.8$ (18.0 h)	672, $k=0.6$ (8.0 h)	12.3 h
JUNE 30	539, $k=2.0$ (10.0 h)	527, $k=1.0$ (3.0 h)	3.7 h
JULY 22	94, $k=5.5$ (24.0 h)	234, $k=6.3$ (10.5 h)	3.5 h
SEPTEMBER 24	254, $k=2.0$ (0.5 h)	291, $k=0.9$ (0.5 h)	0.5 h

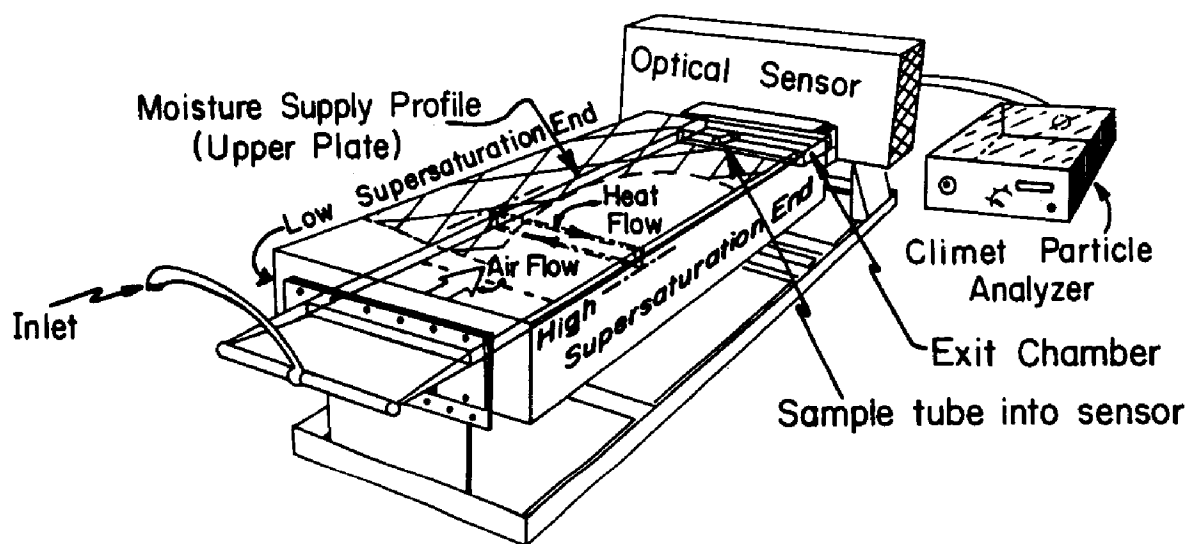


Figure 1 The CCN-Spectrometer.

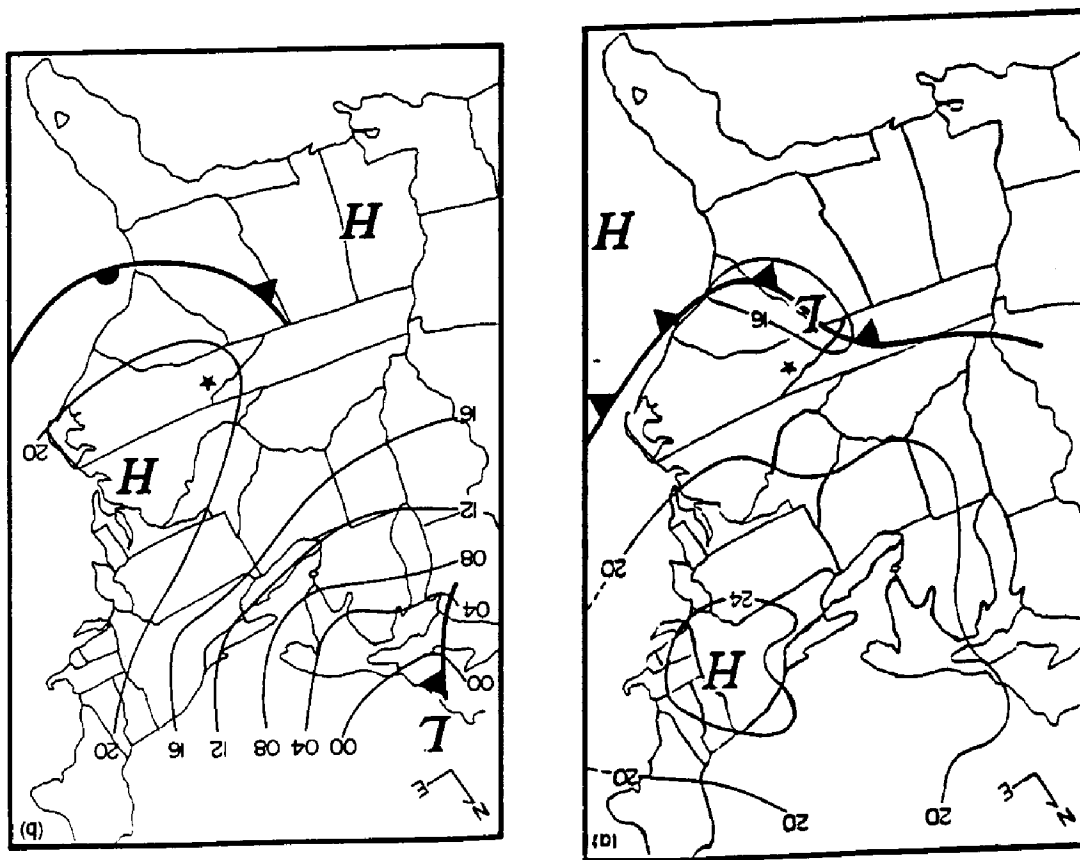


Figure 2 National Weather Service surface charts for 0700 EST June 24 (a) and 0700 EST June 25 (b). The star indicates the location of the Mt. Mitchell State Park, NC sampling site.

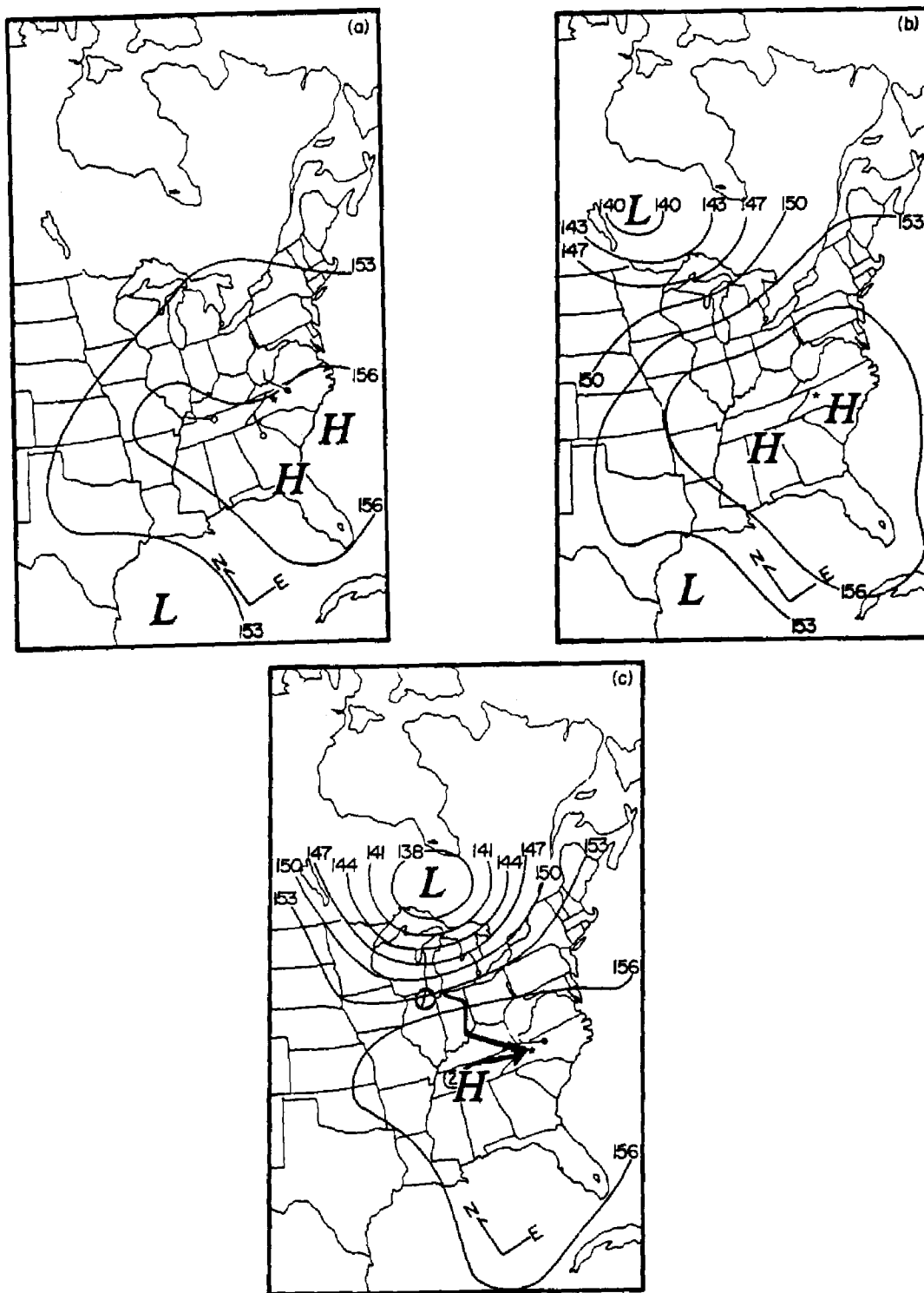


Figure 3 The National Weather Service 850 mb maps for 0700 EST June 24 (a), 1900 EST June 24 (b), for 0700 EST June 25 (c), and the 24-48 h 850 mb back trajectories ending 0700 EST June 24,(2), and 0700 EST,(1), June 25 are shown by the arrows.

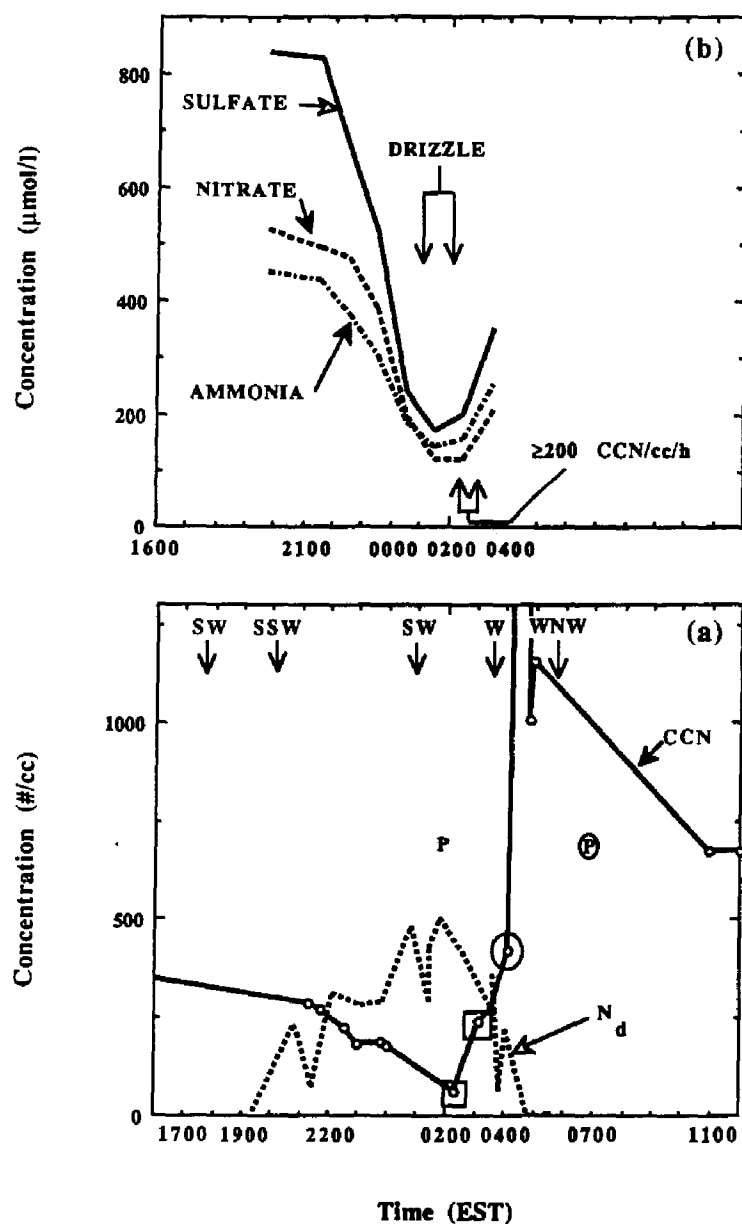


Figure 4 The temporal variations of cloud droplet concentration, N_d , and the cloud condensation nuclei, CCN, concentration (a), and of the predominant cloudwater ions, excluding H^+ , namely, SO_4^- , NO_3^- and NH_4^+ , (b) during the June 24-25, 1988 event. The open boxes indicate the period during which the magnitude of the time rate of change of the CCN concentration is $\geq 200 \text{ cm}^{-3} \text{ h}^{-1}$. The oval represents the same as the open squares, except where evaporation is suspected. The upper case P denotes a 1.0 mb fall in the 0.25 h average atmospheric pressure. The circled upper case P denotes a 1.0 mb rise in the 0.25 h average atmospheric pressure.

POLAR VOLATILE ORGANICS: OVERVIEW OF
PROJECTS OF THE MONITORING METHODS
RESEARCH SECTION - MRB/MRDD/AREAL, U.S. EPA

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The diversity of physical and chemical properties of the various classes of polar volatile organic compounds (PVOCs) requires the application of different monitoring and analytical strategies. Though monitoring methodology for PVOCs at part per million concentrations exists for industrial hygiene applications, these methods are not adequate at ambient concentration levels. The Monitoring Methods Research Section (MMRS) is currently performing or sponsoring research to develop specific methods for the determination of trace levels of PVOCs in an air matrix. These projects include the extension and modification of nonpolar VOCs methodology (Method TO-14) for ketones, epoxides and acrylates; development of novel adsorbents for phenolic and other acidic compounds; real-time methods for formaldehyde; application of new analytical systems such as a glow discharge ion source interfaced to a tandem mass spectrometer, an ion trap system, and a gas chromatograph with atomic emission detector; development of sampling and sample introduction hardware; and development of calibration methods. A brief overview and current status of these projects for PVOCs is presented.

Introduction

The Monitoring Methods Research Section (MMRS) of the EPA Atmospheric Research and Exposure Assessment Laboratory developed EPA's Method TO-14 for the determination of trace levels of specific nonpolar volatile organic compounds (VOCs) in air (1). This methodology is not, however, suitable for what are loosely referred to as the "polar organics" or PVOCs. This diverse grouping of compounds is best characterized by their relative polarity with respect to the hydrocarbons and halogenated hydrocarbons for which TO-14 was developed, or alternatively, the PVOCs are those volatile organics containing atoms such as oxygen, sulfur and nitrogen. These compounds are difficult to deal with at the trace level for a variety of reasons, depending on the specific sub-class. Some tend to be chemically active on metal or other surfaces (in sample tubing, canisters, cryotrap, etc.), and others may be affected by the drying step necessary to remove the bulk of the cocollected water vapor.

The polar fraction of the airborne organic compounds (PVOCs) has been related to high mutagenic and carcinogenic activity, particularly for the semi-volatile and nonvolatile compounds (2-4), and for some specific PVOCs such as formaldehyde (5) and ethylene oxide (6, 7). As such, their trace level determination in air is of interest from a risk assessment viewpoint. Secondly, PVOCs are often implicated as the cause of odor related nuisance complaints from the public (8-13).

Though there exist a variety of industrial hygiene related air methods for high levels of many of the PVOCs, these methods are geared to occupational exposure levels (threshold limit values in the parts per million by volume range) and lack the sensitivity for ambient work, typically by 3 to 5 orders of magnitude. To address the need for determination of PVOCs in ambient air, MMRS has embarked upon a number of projects to develop both sampling and analytical methods for various specific classes of compounds of interest. These classes include, but are not limited to, aldehydes, amines, epoxides, thiols, alcohols, phenols, and isocyanates.

This paper presents an overview of the major research efforts of MMRS that are directed to determination of PVOCs:

- Application of TO-14 methodology to certain PVOCs
- Anion exchange resin as a sorbent for phenolic compounds
- Real-time trace level determination of formaldehyde
- Glow discharge source combined with MS/MS instrumentation for in-situ atmospheric analysis

- Chemical ionization with ion trap detector (ITD) using a water reagent
- Atomic emission detection (AED) coupled to a capillary column gas chromatograph
- Calibration methodology using dynamic and headspace methods
- Valveless GC/MS inlet and preconcentrator

Discussion

TO-14 Extension

The canister sampling methodology for nonpolar VOCs is currently under investigation for extension to certain PVOCs. In-house testing by contractor personnel (NSI Technology Services, EPA Contract 68-02-4444) has shown that over a seven day period the variations in analysis results can be summarized in terms of percentage relative standard deviations (%RSD) of concentration measurements. The listing below is divided into three groups, depending of the range of values of the %RSDs.

Compounds	RSD % N=14
Ethyl acrylate, methyl methacrylate	<3
Acetone, acrylonitrile, isopropanol 2-butanone	<10
Butanol, acetonitrile, ethanol	<23

Samples for these preliminary tests were prepared at the 1- to 4-ppbv level with dynamic dilution of standards from Scott Specialty Gases (Plumsteadville, PA) in a matrix of ambient air. Analyses were performed using standard TO-14 analytical methodology (1) modified to bypass the Nafion tube arrangement used for drying the sample. Only parallel flame ionization and electron capture detectors (FID and ECD) were used to avoid problems with co-collected water vapor. Descriptions of the specific analytical steps are available in TO-14 (1) and other references (14, 15).

This work is now being extended to a larger group of compounds through a research project at Battelle Memorial Institute (Columbus, OH) under EPA Contract 68-D0-0007. In addition to the use of canisters, multisorbent tubes will be used for sampling, and the ion trap detector (Finnegan MAT, San Jose, CA) will be tested for PVOCs applications.

Anion Exchange Resin for Phenolic Compounds

The phenolic compounds are classified as acidic PVOCs. As such, they tend to react in the presence of metal surfaces and dissolve easily in water. A research program was initiated at Battelle Memorial Institute under EPA Contract 68-02-4127 to develop a specific sorbent method for phenolic compounds based upon their acidic properties.

Laboratory work has shown that a strongly basic anion exchange resin AG MP-1 (BioRad Laboratories, Richmond, CA) can be used to quantitatively remove phenols from air and subsequently release analyte ions via an ion exchange mechanism (16, 17). This method to be effective for a variety of phenolic classes. So far, the following compounds have been tested and have exhibited greater than 80% collection/recovery efficiencies:

Phenol	2-NO ₂ -phenol
2-CH ₃ -phenol	3-NO ₂ -phenol
4-CH ₃ -phenol	6-CH ₃ -2-NO ₂ -phenol
2,3-diCH ₃ -phenol	
2-Cl-phenol	2-OH-benzaldehyde
4-Cl-phenol	2-OH-biphenyl
2,4-diCl-phenol	
PentaCl-phenol	

The ultimate goal is to develop a fieldable sampling method based upon resin-filled sorbent tubes that sample at 1 liter/min. Subsequent laboratory analysis would be based upon a negative ion chemical ionization mass spectrometric (NICI-MS) method specific for a group of phenolic analytes. It is expected that this method will allow measurement of a wide variety of phenolic compounds and have sub-part per billion by volume (ppbv) sensitivity.

Real-Time Trace Level Formaldehyde

Various schemes for real-time formaldehyde (HCHO) determinations have been under investigation both at Battelle Memorial Laboratories (EPA Contract 68-02-4127) and as in-house projects by NSI Technology Services (EPA Contract 68-02-4444). These efforts have produced three distinct types of sensitive real-time HCHO monitors; the prototypes are now undergoing rigorous in-house laboratory testing, limited field testing and intermethod comparisons.

The development effort at Battelle has resulted in two different monitor prototypes and two formaldehyde calibration methods. The first monitor relies on an aqueous scrubber for HCHO followed by fluorescence detection of the cyclization product of ammonia, beta-diketone and HCHO (excitation at 254 nm, emission around 520 nm). This prototype has been shown to have a detection

limit of about 0.2 ppbv and a selectivity of 10,000:1 relative to acetaldehyde, and 2,000:1 relative to benzaldehyde (18). The second prototype monitor utilizes a spectroscopic method adapted from commercial SO₂ monitors using direct fluorescence detection (bandpass of 380-550 nm) through UV excitation (bandpass of 280-350 nm) (18). The detection limit of this instrument is currently about 50 ppbv, due to excessive background fluorescence. Optimization of signal to background is planned subject to the results of interference testing. The calibration methods rely upon dynamic dilution of a known HCHO concentration in a stable flow. This known concentration is generated either by the "porous Teflon source," a purged teflon tube immersed in a dilute HCHO solution, or by the "trioxane source," which relies on the sublimation of solid trioxane prior to catalytic conversion to formaldehyde (19).

The in-house effort by NSI personnel produced a prototype portable HCHO monitor based upon the CEA Instruments Model TGM 555 air monitor (CEA Instruments, Emerson, NJ) equipped with the formaldehyde analytical module. This instrument detects 570 nm color development due to the pararosaniline reaction with aqueous formaldehyde in the presence of sodium sulfite. Sample air is drawn into the instrument, scrubbed from the air stream into the pararosaniline-containing aqueous solution and mixed with the reagents. Sulfite is added and color development occurs as the solution passes to the colorimeter. Specific details of the system and its modifications are given in the literature (20). The monitor has been laboratory tested for real-time (with 16 min. delay) operation in the 10- to 100- ppbv range and has been field tested in two indoor air studies.

Glow Discharge-Mass Spectrometer Source

A novel mass spectrometric ionization source is currently under development at the Illinois Institute of Technology - Research Institute (IITRI, Chicago, IL) under EPA Contract 68-D8-0002. This source is a modification of pioneering work on subatmospheric glow discharge ion sources by Glish and McLuckey, et al., (21, 22) at Oak Ridge National Laboratories. The purpose of this work is to utilize the speed, sensitivity and specificity of tandem mass spectrometry for specific application to the PVOCs. The glow discharge, as envisioned, will provide an instantaneous source of analyte ions for presentation to the mass spectrometer. No surface-induced reactions or adsorption is expected to corrupt the sample. The capability of the tandem mass spectrometer for ion separation and filtering obviates the necessity of a separation method such as gas chromatography. The source currently under construction is to be physically compatible with the ITMS mass spectrometer (Finnigan MAT, San Jose, CA) at IITRI. Upon completion, the system will be tested using a variety of PVOC analytes. Future applications include field screening at Superfund sites and

exposure assessment from exhaled human breath analysis. This methodology promises to be generally applicable, but requires the very expensive tandem mass spectrometry capability and will require on-site analysis.

Chemical Ionization Ion Trap Detection

Existing methodology for the nonpolar VOCs requires both drying of the sample and preconcentration of the analytes to achieve adequate sensitivity in conventional quadrupole mass spectrometers (see reference 1, and references therein). The PVOCs pose special problems in such systems; the drying step affects their quantitative throughput for analysis, and a reduction in overall sample, thereby reducing cocollected water vapor, also reduces sensitivity. Secondly, the conventional electron impact sources of quadrupole instruments provide a "hard" ionization that can excessively fragment the light PVOCs, thus reducing the characteristic fingerprint of the molecular ion. To combat both the problem of cocollected water and "hard" ionization, a project that uses chemical ionization (CI) with water as the reagent gas was initiated. The Finnigan Ion Trap Detector (ITD 800, Finnigan MAT, San Jose, CA) was chosen for this project for its high sensitivity and for the relative ease of implementation of water CI. The work was performed at IITRI under EPA Contract No. 68-D8-0002.

This project involves only the analytical portion of PVOCs determination and it is assumed that analytes can be presented to the inlet of the system, either in-situ or via some unspecified sampling medium, without adversely affecting their integrity. Samples were prepared in zero-grade humidified air with a micro-syringe driver, continuous injection system; only laboratory testing was performed. The calibration methodology and the development/evaluation of the ITD-based system are presented in an EPA report (23) and other publications (24,25).

Results indicate that the analytical methodology is appropriate for the PVOCs. The CI capability and the ITD's high sensitivity allow full scan mode spectra at trace levels for many PVOCs. Comparisons of electron impact (EI) spectra and CI spectra show that water CI is much more likely to preserve the high mass (molecular ion, M, or protonated molecular ion, M+1) fragments; therefore, the distinction among similar species is much clearer than for EI. Compounds in this category that have been tested include the following:

ethylene oxide	heptanal
3-octanone	benzaldehyde
acetophenone	ethanethiol
benzophenone	2-methyl-1-propanethiol
acrolein	

Two problems were encountered with this project. Certain compounds were lost in the cryotrapping hardware despite the removal of the dryer, and difficulty with the chromatography in the presence of excess water occurred. In particular, the alkylthiol compounds exhibited low recoveries and some lighter ketones were not well resolved chromatographically. These issues will be addressed in future work through the use of smaller sample sizes and by the addition of novel concentration/injection hardware being developed specifically for the ITD.

Atomic Emission Detector

Though mass spectrometry is generally considered the primary identification tool for gas chromatography, often the identification of unknowns is complicated when similar functional groups or chemical structures (causing similar ionic fragmentation patterns) occur in closely eluting species. Also, mass spectrometric fragmentation can result in neutral group losses that completely obscure the identity of compounds. The atomic emission detector (AED) is a gas chromatographic detector capable of detecting the elemental composition of compounds, regardless of the molecular structure. It operates by energizing GC column effluents in a microwave plasma, thereby reducing the analytes to excited atoms. As the excited atoms relax back to their lower energy levels, they emit light at characteristic frequencies; this radiated energy is dispersed and detected by a photodiode array. Up to four distinct elements can be detected simultaneously with this system. Detailed descriptions of this new instrumentation are available in the literature (26-28). The AED is a complementary detector to an MS, providing confirmatory identification information on atomic constituents not generally possible with mass spectrometry.

An AED system (HP-5921A, Hewlett-Packard, Avondale, PA) has been procured for application to PVOCs analysis and is operated by NSI personnel under EPA Contract No. 68-02-4444 as an in-house project. To date, the instrument has been installed and tested for operation. It is planned to perform trace level work with a variety of PVOCs.

Calibration Methodology for PVOCs

Due to the varied reactivities of the PVOCs, each of the various sub-classes may require a differing calibration methodology at the trace level. The conventional method of dynamic dilution has been tested for a subset of the compounds listed in the section of this document entitled "TO-14 Extension." Further calibration work was performed in-house using modified TO-14 hardware to determine approximate responses and chromatographic parameters for a variety of PVOCs, including:

ethylene oxide	methanol
propylene oxide	trimethyl silanol
2-chloroethanol	acetone
1-butanol	pyridine
acetonitrile	hexamethyl cyclotrisiloxane
acrylonitrile	octamethyl cyclotetrasiloxane
tert-butyl alcohol	vinyl acetate
1-propanol	benzyl alcohol
2-butanone (MEK)	nitrobenzene
ethyl acetate	4-phenyl cyclohexene
tetrahydrofuran	butylated hydroxytoluene (BHT)

This work was presented at the 1989 Pittsburgh Conference (29). Additional in-house work is in progress for calibrating permeation tube devices coupled to dynamic, static, and exponential dilution of samples. The other projects discussed above have their calibration methods presented as part of the cited references.

Valveless GC/MS Inlet

A current, in-house project is to develop a preconcentration interface wherein the analyte cannot contact any surface other than the interior of the column. This is based upon a sampling method reported by Stephens (30) and upon work briefly described at the 1989 ACS meeting by Mouradian, *et al.*, (32) and Arnold, *et al.*, (32).

A prototype inlet system was designed and built to be used with the existing TO-14 equipment (HP-5880 GC and HP-5970 MSD, Hewlett Packard, Palo Alto, CA). The inlet was fully automated and tested, and then applied to a variety of odorous headspace samples including coffee, fruits, consumer products, and plants. Initial tests were successful in detection of the expected PVOCs, when compared to published chromatograms of liquid extracts, or samples collected on other media. As discussed earlier, the sensitivity of this technique using the TO-14 analytical equipment was restricted to analyte amounts in the 100 to 1000 nanogram range because of cocollected water vapor; however, the combination of the valveless GC/MS with the CI-ITD promises to provide the requisite sub-nanogram sensitivity for ambient work.

Conclusions

The projects in progress in the Monitoring Methods Research Section cover a wide variety of topics related to the determination of PVOCs. It is anticipated that a subset of these projects will provide specific methods for general use by the regulatory community, analogous to the acceptance and implementation of the TO-14 methodology for nonpolar VOCs. The MMRS continues to pursue

PVOCs methods development and to support and sponsor scientific exchange through the EPA/AWMA meetings and other similar forums.

Disclaimer

The research described in this article does not necessarily reflect the views of the Agency and no official endorsement should be inferred. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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FOURIER TRANSFORM INFRARED (FTIR) SPECTROSCOPY FOR
MONITORING POLAR AND LABILE AIRBORNE GASES AND VAPORS

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ABSTRACT

The FTIR has been evaluated for monitoring polar and labile airborne gases and vapors. The limit of detection (LOD) for FTIR when using a 10 meter closed path gas cell, a HgCdTe or InSb-MCT detector, 2 cm^{-1} resolution, and least squares fitting (LSF) software is as low as 9 ppb for bis (chloroethyl) ether in air. The LODs for other species, and for these vapors in mixtures, is higher by a factor of up to 100. Software has been developed to identify unknown compounds in the spectra of mixtures of organic vapors.

INTRODUCTION

Efforts in our laboratory have centered on the investigation of the optimal FTIR hardware, software and data base for the near real time qualitative and quantitative analysis of trace levels of airborne gases and vapors (1-7). Much of this work parallels earlier work by Herget (8-10) who has collaborated with us in this present effort, and by Hanst (11).

Air monitoring applications areas have also been delineated by our group, especially in the hazardous waste site monitoring area (12,13). Other groups working with FTIR (14), and with non-FTIR instruments have also defined the needs for instrument development and application for air monitoring (15-17).

It is the purpose of this paper to summarize the results of the efforts in the FTIR air monitoring field ongoing in our laboratory in 1989-90, especially with respect to the limit of detection (LOD) of polar and labile organic vapors.

EXPERIMENTAL SECTION

Samples:

All mixtures of known and unknown samples of vapor mixtures in air were supplied T. Pritchett, U.S. EPA Environmental Response Team.

Hardware:

A Nicolet 20 SXB Fourier transform infrared spectrometer was used with a liquid nitrogen cooled HgCdTe (MCT)-InSb sandwich detector and 10 meter Hanst gas cell. Interferograms were collected to yield spectra of from 0.5 to 8.0 cm^{-1} resolution through deresolution of the 0.5 cm^{-1} interferograms by the method described in previous papers (2-7). Sixty reference standard vapor IR spectra were acquired as a reference library using GC-certified gas cylinders (Scott Specialty Gas Co.).

In addition, a University of Michigan-Nicolet prototype "Baby-ROSE" (Remote Optical Sensing) FTIR has been constructed for applications requiring a transportable system with a pathlength of up to 30 meters. This system has a resolution of 2 cm^{-1} , and operates using an 80386/387 PC and Nicolet-PC software.

Software:

For the detailed theory of LSF software, see papers by Haaland, et al (18,19). Detailed discussions of the

application of LSF software to quantitative analysis of trace gases in ambient air have also been published (2-7).

In addition, to quantitative analysis with LSF, qualitative analysis was also performed using modified Nicolet LSF software. This software performs iterative LSF (ILSF) necessary for qualitative analysis.

DISCUSSION

Examination of the calibration spectra of polar and labile compounds was made after dilution to 10 ppm, 1 ppm, 100 ppb and 10 ppb using a precision dilution manifold after the design of Herget (1) as modified by Strang (2,3). Investigation of the optimal treatment of the data to obtain the lowest possible LOD was made by Strang (3).

Strang determined that, except for hydride gases, a resolution of 2.0 cm^{-1} was optimal. Not only is there no need for higher resolution, but higher resolutions are counter-productive in that they require more expensive and larger instruments, as well as longer computational time and data storage capacity. However, for the hydride gases, resolution of as high as 0.5 cm^{-1} may be needed.

The spectra of some of the polar and labile compounds investigated in this study are shown in the figure.

The question of LODs obtainable using FTIR for compounds in mixtures of up to 12 components was also addressed by Ying (5,6). In most cases, there is a serious degradation in LOD for each component of the mixture. For example, benzene, in a 12 component solvent test mixture, has an LOD in the range of 1-2 ppm. However, certain analytes are less affected or unaffected by the presence of solvent mixtures. This includes some of the Freons as well as the hydride gases (2,3).

The result of determination of LODs for a few polar and labile compounds is given below. The library of spectra compounds in our files approximately numbers 70, over half of which are polar. All spectra have been acquired at 0.5 cm^{-1} resolution, and all are at certified concentrations, or dilutions of those concentrations. All dilutions were performed using an orbital welded, electropolished dilution system with precision pressure/vacuum control.

Compound	Limit of Detection(a)	
	(ppb)(b)	(ug in beam)(c)
acetone	80	0.7
acetaldehyde	39	0.4
acrylonitrile	70	0.4
arsine(d)	8	0.06
benzene	28	0.2
bis (chloroethyl) ether	9	0.1
chlorobenzene	60	0.7
3-chloropropene	50	0.4
o-chlorotoluene	95	1.2
2-butanone	23	0.2
diborane(d)	25	0.07
o-dichlorobenzene	140	2.1
1,4-dioxane	16	0.1
2-ethoxyethanol	32	0.3
ethylene oxide	37	0.2
isopropanol	20	0.1
nitrogen trifluoride	20	0.1
phosphine(d)	60	0.2
propylene oxide	100	0.6
pyridine	830	6.7

(a) LOD for individual compound in ambient air; LOD for multi-component mixtures must be determined for each mixture, and are likely to be 2-100 times higher.

(b) LOD for the indicated concentration in ppb @ 10 meter path length.

(c) Weight of analyte in beam, assuming a total of 2.5 liters actually in beam path in cell used for calibration.

(d) Requires an InSb/MCT detector. All other compounds require only a MCT detector.

Since the LOD is actually proportional to the product of pathlength X concentration, longer path, remote sensing (ROSE) systems may have lower LODs. In addition, these LODs may be improved through the use of improved LSF software with calibration included for the 41 organics listed as target trace atmospheric gases by the EPA-RTP. The use of iterative least squares fitting (ILSF) methods allows both qualitative and quantitative analysis to be accomplished under certain circumstances.

A description of the utility of the FTIR for air monitoring, especially when contrasted to commercially available filter-based systems, has also been published.

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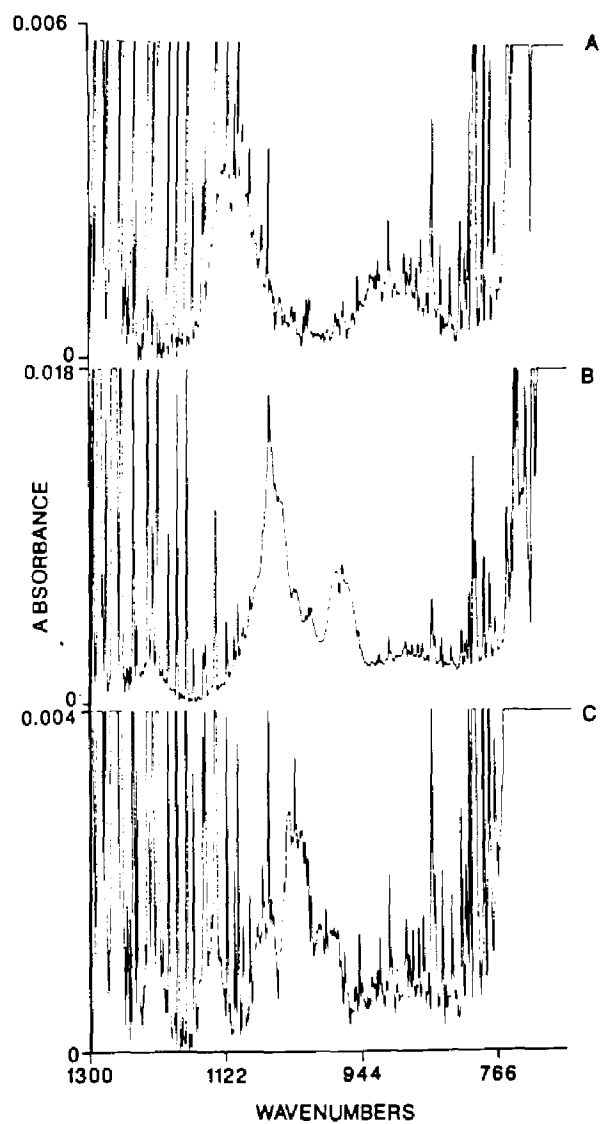


Figure. Spectra of Acetaldehyde (A), N-Propanol (B), and Pyridine (C) at 5 ppm in Ambient Air.

OPTIMIZATION OF ANALYTICAL PROCEDURE FOR CHARACTERIZING
AMBIENT POLAR VOLATILE ORGANIC COMPOUNDS

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The analysis of ambient levels of volatile organic compounds (VOCs) in air usually involves cryogenic trapping of the analytes, followed by thermal desorption and low-temperature refocussing onto a column for analysis by high-resolution gas chromatography and electron impact mass spectrometry (GC/MS). This approach has been widely used for nonpolar VOCs, but the ambient water vapor co-collected with the sample causes problems which have prevented its use for more polar species.

Preliminary experiments have indicated that chemical ionization (CI) GC/MS with the Ion Trap Detector™ (ITD) using water, including the water present in the air, as the CI reagent is suitable for the measurement of polar VOCs in whole air samples. Chemical ionization of the water gives intense pseudomolecular ions for various polar compounds and enhanced sensitivities in comparison with electron impact data. These experiments also showed, however, that delivery of the compounds to the GC/ITD for analysis, as well as calibration of the system, are aspects which demand attention. Recent work has accordingly focussed on developing and testing such methods for the generation of experimental data to evaluate the approach for several target polar compounds of interest, including alcohols, ketones, and thiols.

Introduction

The need to develop better measurement techniques for polar volatile organic compounds of low molecular weight has been spurred by increasing public concern over these compounds. Certain polar VOCs (e.g., alkyl-thiols, amines, aldehydes, etc) are often the subject of nuisance complaints from the public, while others (e.g., ethylene oxide, propylene oxide, acrolein, etc) are sometimes cited as potentially toxic compounds from industrial emissions. However, the analysis of trace levels of polar VOCs in air poses many problems, and the nature and distribution of these compounds in the atmosphere cannot be adequately characterized at present.

The measurement of nonpolar VOCs in air is well established using polished stainless steel sampling canisters together with cryogenic trapping and gas chromatography/mass spectrometry.¹ Cryogenic trapping preconcentrates the analytes by condensing them on the cold surface of the trap, after which they are desorbed and flushed onto the GC column for analysis. Co-collected water vapor is dealt with by passing the sample through a Nafion membrane dryer before it enters the GC.² This technique is, however, not generally applicable to small polar molecules since they permeate the walls of the dryer tube along with the water vapor, and are consequently lost.³

Most methods used to measure polar VOCs in air stem from industrial hygiene technology, and rely mainly on liquid impinger sampling. As a result, they are generally restricted in sensitivity to ppmv levels. Most efforts to sample polar VOCs at trace levels have been largely ineffective due to their greater chemical reactivity, affinity for surfaces, and tendency to undergo polymerization.³

In a recent report, we proposed the use of chemical ionization GC/MS in the quadrupole ion trap as a promising method for measuring polar VOCs in whole air samples.⁴ The approach makes use of the water vapor present in the air as the CI reagent. We showed that water is an effective CI reagent gas in the ion trap, and reacts with high sensitivity with a range of polar compounds. This paper describes an extension of this work in which we have explored conditions for the use of GC/water CI-ITD, in the full scan mode, for the analysis of selected polar VOCs in whole air samples.

Experimental Methods

The system used was a cryogenic sampling unit (Nutech 3538-02) coupled to a Varian 3400 GC and Finnigan MAT 800 ITD (Figure 1). Analyses were performed using a nonpolar 30 m x 0.53 mm ID HP-1 methylsilicone column (0.88 μ m film thickness), the outlet of which was connected to the ITD via a heated transfer line. The ion trap was controlled by a COMPAQ DESKPRO™ 386/20 personal computer using Automatic Reaction Control™ software for CI supplied by the manufacturer. For the CI experiments, water in a reservoir attached to the reagent gas inlet port was used to augment the water concentration in the ion trap and maintain a constant reagent gas pressure.

The test atmospheres used in this study were supplied by a vapor generator system and included ketones, alcohols, thiols, nitrobenzene, and three nonpolar compounds. The vapor generator is shown in Figure 2. It made use of a SAGE micro-syringe pump and was designed to produce constant concentrations of the compounds in dry or humidified air. The air was humidified by first passing through a flask partially filled with water.

For all of the experiments described here, the relative humidity was adjusted to about 35%. The output of the syringe was attached to a heated septum, and the vapor concentration was carefully controlled by the appropriate choice of flow rates of the air and the liquid mixture from the syringe.

In order to check the response of the analytical system, the vapor generator was calibrated using a sorbent preconcentration technique. These measurements were made by connecting a Tenax cartridge at the outlet from the vapor generator to the cryogenic trap. The gas flow through the cartridge was maintained at 20 cm³/min, the flow rate of air typically used when collecting a sample in the cryogenic trap. At the end of the 10-minute sampling period, the Tenax cartridge was removed and analyzed by a standard thermal desorption GC/MS technique.⁵ The GC/MS was calibrated using Tenax cartridges loaded with the test mixture from a flash evaporator.

Results And Discussion

The calibration experiments showed that Tenax cartridges together with thermal desorption GC/MS analysis provide an effective and independent method for measuring the concentrations of the selected polar compounds at the outlet of the vapor generator. The peak area measurements for the polar compounds loaded directly onto Tenax cartridges by flash evaporation show a level of precision ($\pm 10\%$ relative standard deviation) comparable to that obtained for nonpolar compounds by this technique.⁵ The same approach was used to establish the peak area reproducibility at the outlet of the vapor generator. Although the precision for the polar compounds is not as high as before ($\pm 16\%$ relative standard deviation), the values are nevertheless still quite acceptable and similar to those for the nonpolar compounds in the test mixture.

In order to evaluate the trapping and recovery efficiency of the cryogenic interface, the vapor generator was attached to the interface and samples were collected on Tenax cartridges at the cryotrap outlet. The cartridges were again analyzed by thermal desorption GC/MS. The results are presented in Table 1. The recoveries obtained are very good for all of the compounds, except for the thiols and naphthalene. These results indicate that the water vapor present does not have a deleterious effect on the behavior of these polar compounds in the cryotrap. The hot surfaces to which the compounds are exposed within the cryotrap during the transfer operation to the cartridges may be responsible for the virtual disappearance of the thiols. The low recovery measured for naphthalene is somewhat surprising in view of its lack of polarity.

The final consideration in these tests was that the water vapor in the humidified air stream might have an adverse effect on analytical performance. To explore this possibility, the output from the cryogenic interface was attached directly to the GC/CI-ITD system and the experiments were repeated. The results are also included in Table 1. An examination of the data shows that, in contrast to the previous situation, all of the measured recoveries are very low, except for the nonpolar compounds and nitrobenzene. The alcohols in the test mixture gave "smeared-out" peaks which could not be quantitated. These low recoveries indicate a severe humidity effect on chromatographic performance when the water vapor in the sample is allowed to pass directly to the GC column.

One way of reducing the deleterious effect of water vapor on chromatographic performance may be to decrease the sample size and take

advantage of the high sensitivity of the ITD in the water CI mode.⁴ To test this approach, the vapor generator was adjusted to give a test atmosphere containing the VOCs at a constant concentration, and experiments were performed in which the volume of air sampled in the cryogenic trap was systematically decreased from 250 cm³ to 50 cm³. The results are presented in Figure 3 for the polar compounds nitrobenzene, acetone, and 1-butanol, and the nonpolar p-dichlorobenzene. Except for 1-butanol, which shows a fairly rapid decrease in signal response with sample volume, the plots for the remaining polar compounds suggest that it is feasible to use much smaller samples with water CI-ITD as a means of reducing the adverse effects of water vapor on system performance.

Conclusions

The ITD has several features that combine to make it an ideal detector for the analysis of polar VOCs in air. Among these, the most important are its chemical ionization capability and its high sensitivity in the full-scan mode. This study has shown that whole-air samples can be effectively analyzed with the ITD by exploiting the water vapor present in the air, and a number of polar compounds can be transferred through the cryogenic preconcentrator without significant loss. Although the water vapor seriously degrades chromatographic performance, this problem can be alleviated to a large extent by using smaller air samples and taking advantage of the ion trap's sensitivity.

Disclaimer

Although the research described was funded by the U.S. Environmental Protection Agency through Contract 68-D8-0002 to IIT Research Institute, this document has not been subjected to Agency review and does not necessarily reflect the views of the Agency. No official endorsement should be inferred by its inclusion in these proceedings.

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Table 1. Recovery of polar and nonpolar compounds in air from cryogenic trap, measured using Tenax cartridges and by direct analysis with GC/ITD

Compound	Percent Recovery ^a	
	Cryotrap-Tenax	Cryotrap-GC/ITD
Acetone	117	nq ^b
1-Propanethiol	12	12
2-Methyl-1-Propanethiol	1	25
2-Butanone	103	44
2-Propanol	125	nq
Ethanol	119	nq
1-Butanethiol	nd ^c	4
1-Butanol	103	nq
Nitrobenzene	92	99
1,1,1-Trichloroethane	123	59
p-Dichlorobenzene	103	114
Naphthalene	57	105

^a Average of three experiments.

^b nq = Not quantitated; peak observed but "smeared-out"

^c nd = Not detected

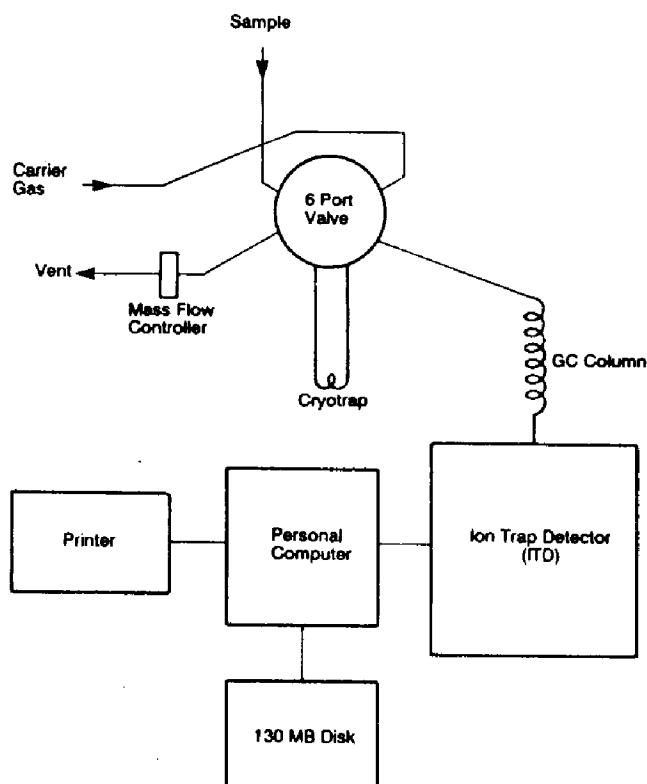


Figure 1. Cryotrap and GC/CI-ITD system for analysis of VOCs in air.

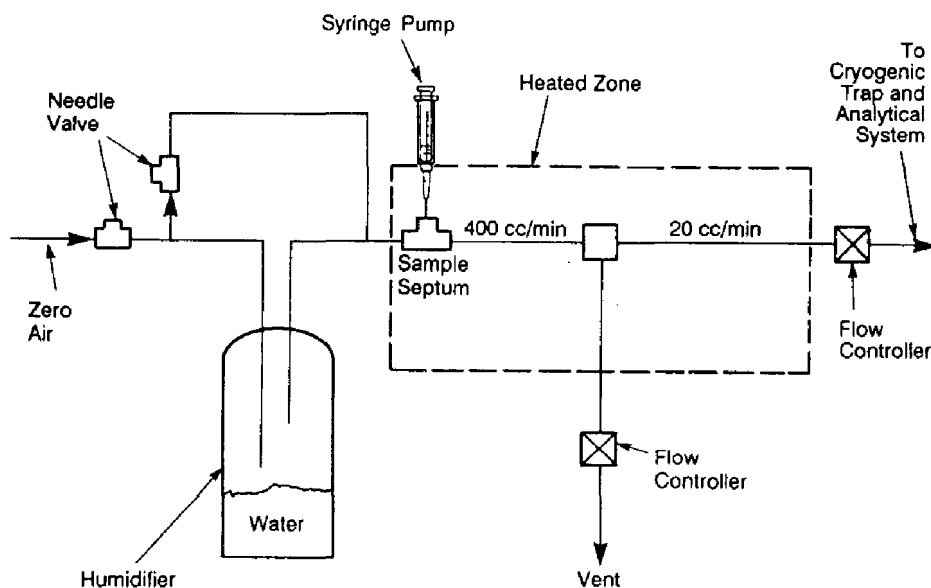


Figure 2. Schematic of vapor generator.

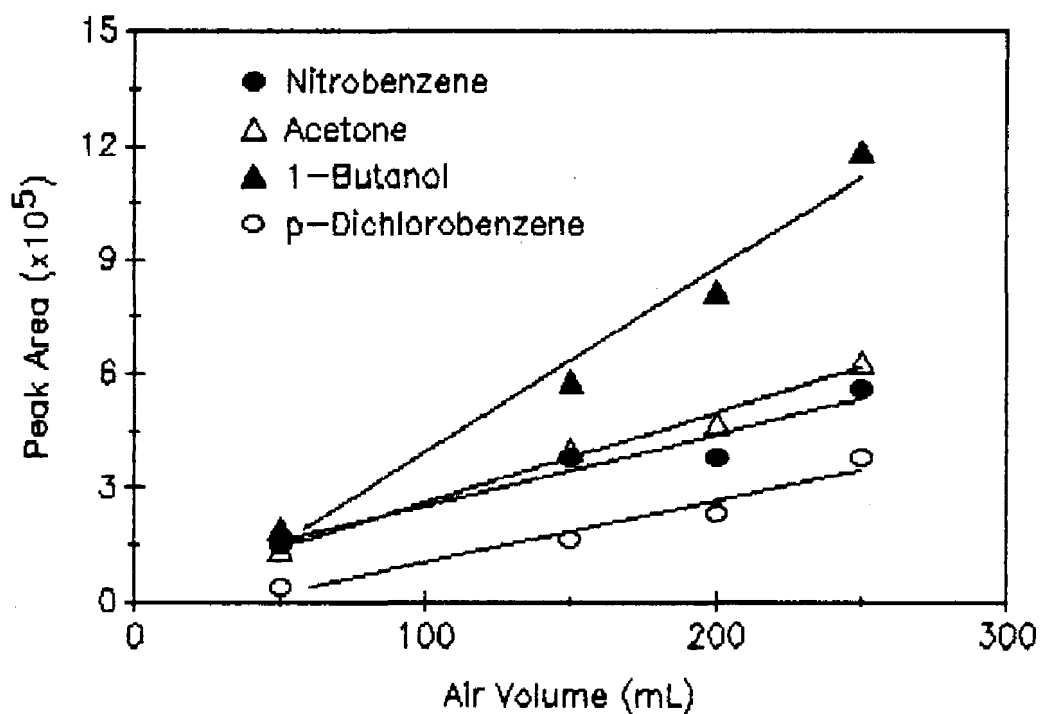


Figure 3. Variation of peak area with sample volume for selected polar and nonpolar VOCs.

ANALYSIS OF POLAR SEMIVOLATILE ORGANIC COMPOUNDS BY LIQUID CHROMATOGRAPHY/MASS SPECTROMETRY

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Nonpolar semivolatile organic compounds (SVOCs) are routinely analyzed by gas chromatography/mass spectrometry, but the technique has severe limitations when polar SVOCs and nonvolatile organic compounds are the analytical targets. Polar compounds may present difficulties due to thermal instability, insufficient volatility, and adsorption in the chromatographic system, creating a need to develop methods based on liquid chromatography/mass spectrometry (LC/MS). Experiments involving the analysis of polar derivatives of polycyclic aromatic hydrocarbons by particle beam LC/MS demonstrate the ability of the instrument to generate useable electron impact and electron capture negative ionization spectra for some compound classes and illustrate the problems associated with analysis of hydroxy-aromatic compounds.

Introduction

The need to analyze airborne particulate matter for polar organic compounds has been demonstrated by groups working with bioassay-directed fractionation, who have found substantial mutagenic activity in the polar fractions of extracts.¹ The difficulties inherent in gas chromatographic (GC) analysis of polar semivolatile organic compounds (SVOCs; i.e., thermal instability, adsorption, and insufficient volatility) have hindered efforts to characterize these polar fractions, spurring our interest in liquid chromatography/mass spectrometry (LC/MS).

We are currently evaluating a commercial particle beam LC/MS system for use in the analysis of polar SVOCs, especially substituted polycyclic aromatic hydrocarbons (PAHs), in airborne particulate matter. The particle beam interface, developed by Willoughby and Browner² and improved by Winkler *et al.*,³ is based on a two-stage momentum separator. The LC effluent is nebulized in a stream of helium, and the solvent evaporates from the droplets in a desolvation chamber at reduced pressure. The solvent vapor and analytes then pass through the momentum separator, where most of the solvent is pumped away, and the analytes are transferred to the ion source of the mass spectrometer as a stream of dry particles. The apparent advantage of the particle beam interface is solvent removal without exposure of the analytes to heated surfaces, which might cause decomposition of sensitive compounds. Solvent removal allows the use of the standard modes of ionization, including electron impact (EI) and chemical ionization (CI) in an unmodified MS ion source.

This paper highlights the results of our preliminary studies with polar PAH derivatives. We have examined optimization of the particle beam operating parameters and investigated the potential for analysis of substituted PAHs by both EI and electron capture negative ionization (ECNI) LC/MS.

Experimental Methods

All experiments were performed on a Hewlett-Packard (HP; Palo Alto, CA) 5988A mass spectrometer equipped with a switchable EI/CI ion source, negative ion detection, and an HP 59980A particle beam LC/MS interface. Negative ion experiments were performed with either methane or carbon dioxide to moderate the gas introduced through the particle beam interface. The high-performance liquid chromatograph (HPLC) was an HP 1090 with ternary-gradient solvent delivery system and a diode array detector, which was used in line with the particle beam interface. The HPLC columns were Brownlee Labs (Santa Clara, CA) 10-cm x 2.1-mm Spheri-5 cyano columns with 5- μ m particles. The mobile phase flow rate was 0.3 ml/min.

Results and Discussion

There are several operational parameters which can be adjusted to optimize the performance of the particle beam LC/MS for a specific analysis. These are (1) LC mobile phase composition, (2) interface variables (nebulizer gas flow, nebulizer capillary position, and desolvation chamber temperature), and (3) ion source temperature. The dependence of sensitivity on mobile phase composition was noted by Willoughby and Browner.² We have confirmed that, for PAHs, organic solvents yield better sensitivity than water-organic blends and that hexane and methanol yield slightly better sensitivity than acetonitrile. Hexane and acetonitrile produce slightly less chromatographic peak tailing than does methanol. The optimum nebulizer capillary position is highly dependent on both the analyte and the solvent composition, whereas the nebulizer gas flow is less so, and both must be determined

experimentally. The desolvation chamber temperature does not appear to be a critical variable. The ion source temperature has strong effects on sensitivity, chromatographic peak shape, and spectral profile for the PAH derivatives in both the EI and CI modes; temperatures of 250°C to 300°C are optimum for EI operation with compounds up to molecular weight 300. At lower temperatures, sensitivity is reduced, and the less volatile compounds show chromatographic peak tailing.

We have obtained EI and ECNI spectra of a variety of substituted PAHs, including hydroxy-, nitro-, and amino-PAHs, and benz[a]acridine. The EI responses for hydroxy-PAHs are considerably weaker than for nitro- and amino-PAHs and unsubstituted PAHs. At an EI source temperature of 300°C, there may be considerably more fragmentation than found in GC/MS or standard library spectra for some compounds. Under these conditions, the nitro-PAHs produce little or no molecular ion signal (Figure 1).

The CO₂-ECNI spectra of nitro-PAHs are more predictable, containing primarily molecular ions and small [M-O]⁺ peaks (Figure 2). The limit of detection for the nitro-PAHs is approximately 1-2 ng by selected ion monitoring and 10 ng full scan, but the response under all conditions is nonlinear, severely curtailing the potential for quantitative analysis.

The hydroxy-nitro-PAHs tested by ECNI were not detected at levels from 100 to 150 ng. That is consistent with the poor performance of the interface with other hydroxy-aromatics. Hydroxy-PAHs, pentachlorophenol, and Dinoseb all show reduced response relative to the nonhydroxylated analogs. For example, the EI detection limit for pentachlorophenol is approximately 2.5 µg on column versus 20 ng for pentachlorobenzene. In addition, the hydroxy-PAHs show significant tailing and carry-over, indicative of adsorption in the particle beam interface, which could not be alleviated by addition of acetic acid to the mobile phase.

Conclusions

The particle beam LC/MS can generate useful EI and ECNI spectra of PAHs and substituted PAHs, although the degree to which the EI spectra match the reference libraries is variable. The difficulty in analyzing hydroxy-aromatic compounds indicates the need for further development of the particle beam interface.

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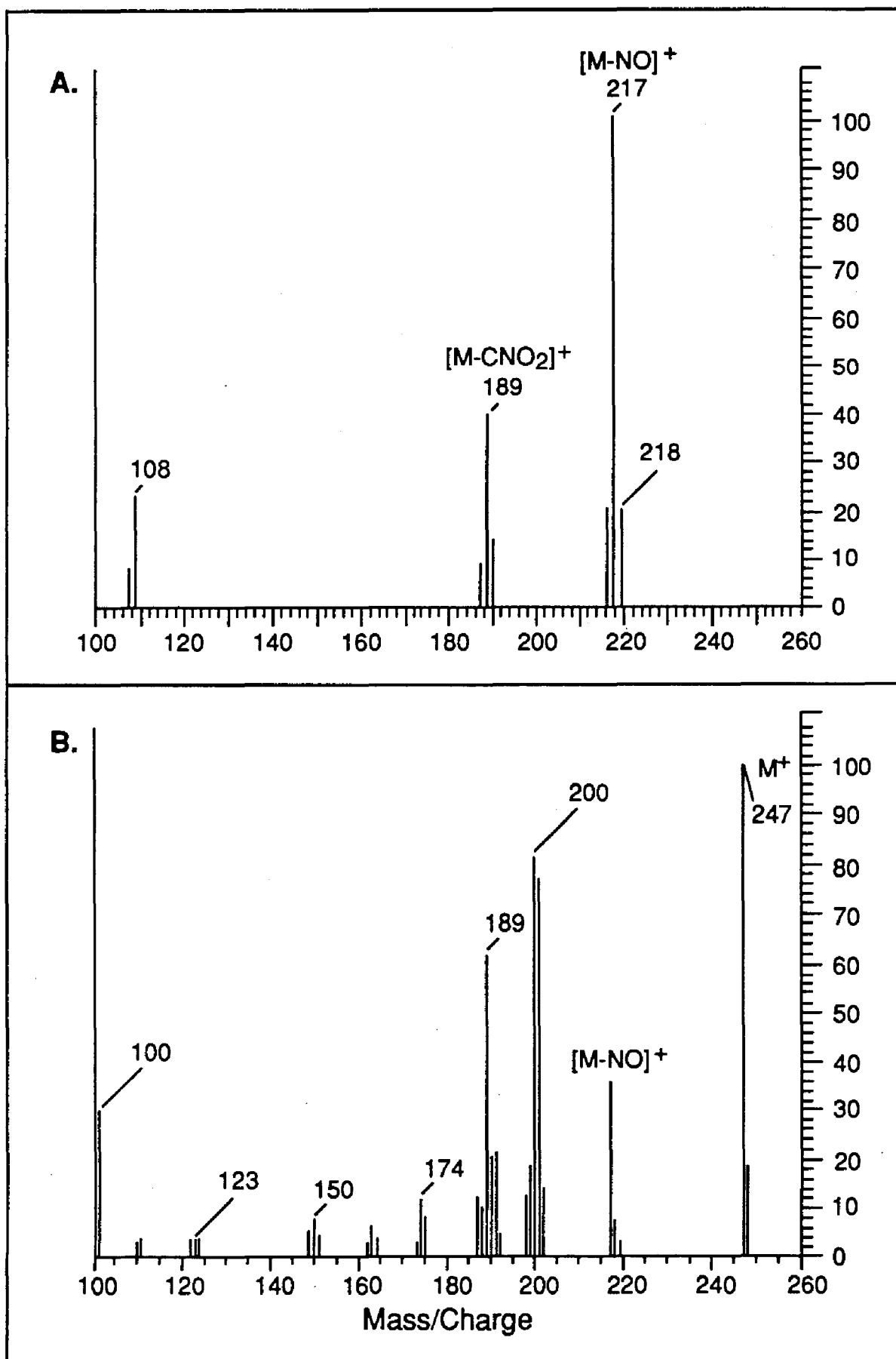


Figure 1. EI mass spectra of 3-nitrofluoranthene. A. LC/MS. B. GC/MS.

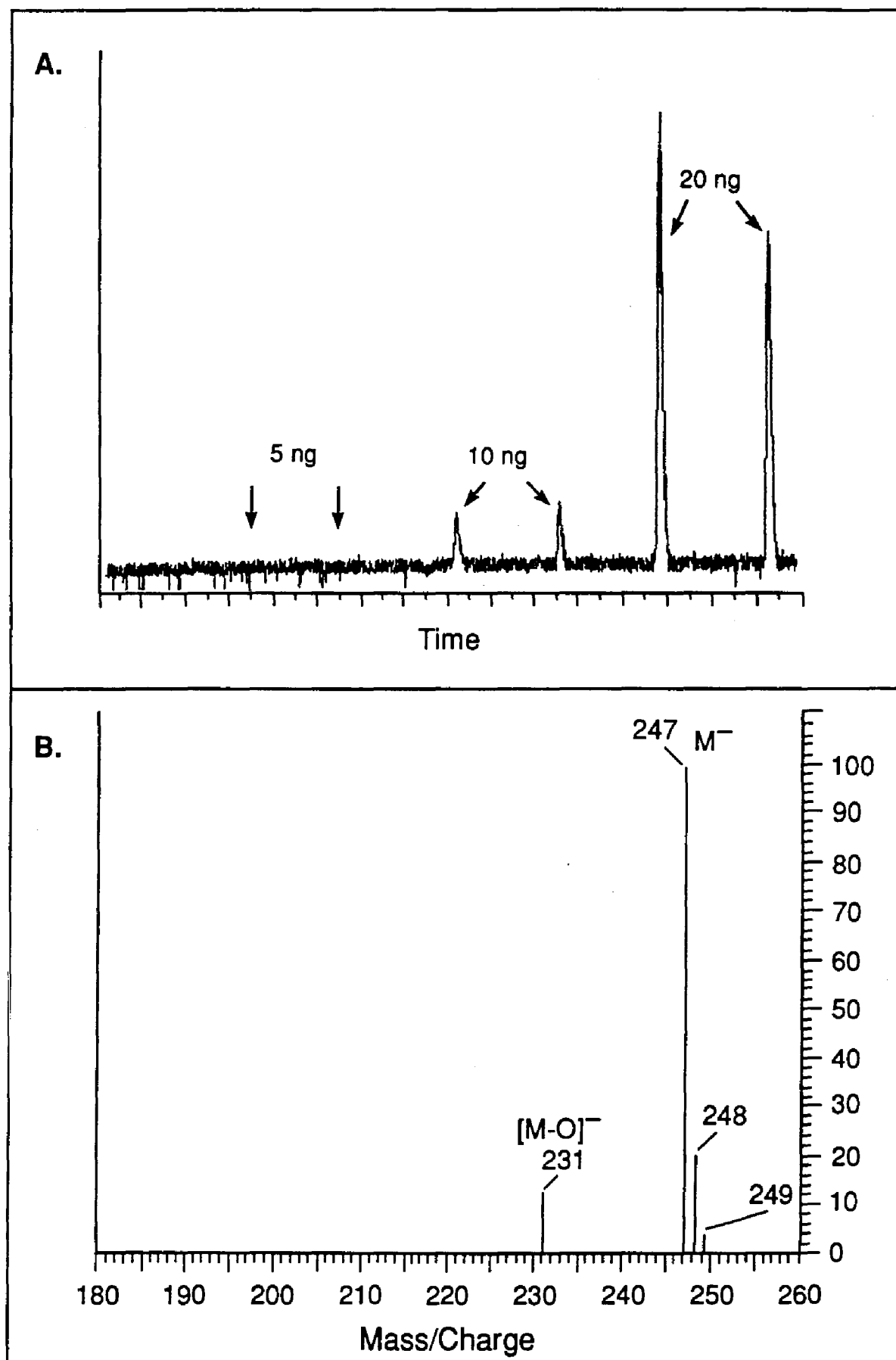


Figure 2. A. ECNI-LC/MS TIC of repeated injections of 3-nitrofluoranthene.
B. Mass spectrum of 20 ng of 3-nitrofluoranthene.

ANALYSIS OF VOLATILE ORGANICS IN AIR
VIA WATER METHODS

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A modified compendium method TO14 for volatile organic compounds in air is used in the EPA Region IV laboratory. This method is a combination of EPA volatile organic water methods (i.e. 524.2, 8240) and method TO14 for the analysis of air canisters. A standard water purge and trap device with a solid sorbent trap is used. Air standards containing 63 analytes plus 3 internal standards and 3 surrogates are prepared in canisters using the water method purging vessel. The analysis is by a gas chromatograph/mass spectrometer (GC/MS) operating in full scan mode. Cryofocusing of the gas chromatograph oven is necessary only for analysis of the very volatile gases.

Introduction

The EPA Region IV laboratory has been involved in the analysis of volatile organics in water and soil/sediment samples for more than ten years. These analyses are performed by standard EPA protocols for programs such as NPDES permits, drinking water regulations, and OSWER regulations. Recently the laboratory was requested to analyze this same group of volatile analytes in air samples. All of our GC/MS systems were devoted to the analysis of samples from other media; therefore, a protocol was developed to utilize existing instrumentation to perform these analyses with a minimum of disruption. It was decided that using 6 liter air canisters and Compendium Method TO14 with minor modifications would best meet Region IV's immediate needs. Four separate techniques were developed for the entire analytical system. These involved cleaning canisters for laboratory blank, standard, and audit material use; preparing standards mixtures in canisters; sample canister preparation for analysis; and developing the analytical system. (See Figure 1 and Figure 2 for an overall view of the analytical system.)

Experimental

Canister Cleaning Procedure

The most effective and time efficient canister cleaning technique involves a two stage process. The following equipment was used:

1. A direct drive mechanical pump with a free air displacement of 9 m³/h with molecular sieve trap on the inlet side of the pump.
2. A rheostat controlled hot plate.
3. An ultra high purity nitrogen cylinder with a stainless steel diaphragm and a humidifier vessel plumbed in the line to the canister with 1/16 in. stainless steel tubing.
4. A 0-1500 mm Hg air gauge calibrated to read Absolute pressure.

The canister is first evacuated to less than 25mm Hg Absolute. Then it is pressurized with humidified nitrogen to 1500 mm Hg. The canister is then placed on a warm hot plate and evacuated for 15 minutes. The canister is pressurized again, then re-evacuated for another 15 minutes while still on the hot plate. The canister is removed from the hot plate, pressurized to 1500 mm Hg, then re-evacuated until the canister is cool (approx 15 min). The canister at this point should read less than 25 mm Hg and is held under vacuum until used.

Calibrated Standard Canister Preparation

Utilizing knowledge gained from sparging volatile organic analytes from water samples onto a purge and trap system, a sparging system was developed to purge these same volatile organics from water into an air canister. The following equipment was used for preparing analytical standard mixtures of volatile organics in canisters:

1. Zero grade air cylinder with stainless steel diaphragm and 1/16 in. stainless steel tubing.
2. A 5 ml needle sparging vessel, used in sparging water samples, plumbed with 1/16 in. stainless steel tubing to a pressure flow controller on the nitrogen cylinder used in canister cleaning.
3. Standard solution of volatile organics in methanol (currently a 63 analyte mix).
4. A methanol solution containing 3 internal standards and 3 surrogates.
5. 6 liter stainless steel air canister.
6. 5 ml gas tight syringe.
7. 25 ul gas tight syringe.
8. Heat wrap for sparge vessel.

A previously cleaned canister still under vacuum is pressurized to 760 mm

Hg Absolute (1 atm) with zero grade air. The air gauge is removed from the canister and the sparging vessel is connected to the canister with the shortest length of 1/16 in. stainless steel tubing possible. (Extra efforts were made to minimize possible areas of dead volume to maximize transfer of analytes from the water to the canister.) Five milliliters of water is spiked with the standard solution and the internal standard/surrogate solution. This water is transferred into the sparge vessel and the water is purged with nitrogen for 10 min at 100 cm³/min while being heated at 40 °C. At the end of 10 minutes the sparge vessel is removed from the canister, the air gauge re-installed and the canister is pressurized with pure nitrogen to 1500 mm Hg Absolute (approx 15 psi). The canister is allowed to equilibrate overnight before use. (See Figure 3 for an overview of the canister preparation technique.)

Sample Canister Preparation

The sample collection protocol requires that the canisters return to the lab at near but less than 760 mm Hg Absolute (approx 1 atm). At this point the sample canister is prepared as the standard canister is, starting after the pressurization to 760 mm Hg with air. The one exception is that the 63 analyte standard mixture is not added to the water; only the internal standard/surrogate solution is added. Samples are allowed to equilibrate a minimum of 2 hours after pressurizing before analysis. (See Figure 4 for results of equilibration study.)

Analytical System Description

The analytical system is a combination of EPA volatile organic water methods (i.e. 524.2, 8240) and method TO14 for the analysis of air canisters. A standard water purge and trap device with a solid sorbent trap is used. The analysis is by a gas chromatograph/mass spectrometer (GC/MS) utilizing a capillary column and operating in full scan mode. Cryofocusing of the gas chromatographic oven with liquid nitrogen is necessary if the analysis of the very volatile gases is required. The following equipment is used:

1. Automated water and soil/sediment purge and trap equipment.
2. Solid sorbent trap consisting of two hydrophobic adsorbent beds (200 mg Carbopack B and 50 mg Carbosieve S-III, both 60/80 mesh) which minimize water vapor collected during the canister subsampling.
3. Heated transfer line (1/16 in. stainless steel tubing with 1/16 in. stainless steel tee at canister end).
4. GC/MS system with 60 m megabore column, liquid nitrogen cooling, and full scan mass spectrometer mode.
5. Small diaphragm type vacuum pump (approx 0.25 m³/h displacement).
6. Mass flow controller calibrated to handle up to 100 cm³/min.

A transfer line heated to approx 100 °C is connected to the purge outlet on one of the ports of the automated purge apparatus. A 1/16 in. stainless steel tube is connected on one end to the purge flow inlet of the automated purge apparatus and on the other end to a cut-off valve at the tee on the canister end of the heated transfer line. The tee is connected directly to the canister with an adaptor fitting. The trap vent outlet on the purge and trap system is connected to a mass flow controller set at 100 cm³/min. The small vacuum pump is connected downstream of the mass flow controller to maintain a positive pressure differential across the flow controller. (See Figure 2 for an overview of the analytical system.)

Air Canister Analysis

The cut-off valve on the purge inlet line should be closed during the purge mode but open during the desorb and bake modes. This flow flushes the transfer line during the bake cycle. With the mass flow controller

set to allow a flow of 100 cm³/min, the canister valve is opened and the purge mode is started on the purge and trap system. The purge mode is maintained for 10 min giving a total volume of 1000 cm³ (1 liter). The trap temperature is maintained at less than 30°C during the purge mode. The gas chromatographic oven is cooled to -50°C and the desorb mode is started. The oven is programmed up to 180°C at 8°C/min. The mass spectrometer is scanned from 35-300 amu at 1 amu/sec. A standard curve is generated from canisters prepared from a concentration range of 5 ug/m³ to 150 ug/m³. A daily standard is analyzed at 50 ug/m³. This daily standard is compared to the original curve as a quality control measure. Internal standard response is monitored throughout the day and surrogate recoveries are monitored in every analysis. A laboratory blank canister is analyzed daily to monitor laboratory contamination. The quality assurance measures used in the Superfund Contract Laboratory Program statement of work for multi-level multi-media are followed very closely.

Results

The precision of the method including canister preparation was demonstrated to be equivalent to the EPA water methods based on seven replicate analyses. The highest %RSD of the seven replicates of the 63 analytes was 7.3 for methyl ethyl ketone. These seven replicates came from three separate canisters prepared at nominally 50 ug/m³ per analyte. The curve data was equally good with only one analyte having a %RSD greater than 20 (1,1,2-trichloroethane, 21 %RSD) in the curve. The %RSD of the majority of analytes was less than 10. (See Figures 5 & 6.)

Laboratory blank analysis continues to be a problem area at the 5-20 ug/m³ range for a few compounds. Acetone and methyl ethyl ketone are persistent contaminants in the reagent water used for sparging and humidifying the canisters. Naphthalene tends to carry over from high concentration samples (>50 ug/m³) into the next analysis. Extra efforts must be made to eliminate higher boiling point analytes from the system.

Five audit canisters prepared by EPA, RTP were analyzed to determine accuracy. (See Figures 7 & 8.) Of the 28 analytes present in the audits only 3 could be considered outside of normal quality control ranges. Vinyl chloride in two of the audits was in the 125-150 % recovery range. The problem with this data was caused by an inaccurate concentration in the methanol solution used to prepare the standard canister and not by the air analysis. Acetone and methyl ethyl ketone were in the 150-300 % recovery range. This is not surprising since the audits were in the 10 ug/m³ range and the laboratory blanks contain 10-20 ug/m³ of these analytes. With a purer quality of water, these analyte results should improve.

Conclusion

This method allows Region IV to utilize the same instrumentation for air, water, and soil analyses. The target analyte list is the same for the different media and includes several "polar" water soluble organic compounds. The potential of switching analyses between media on the same instrument with minimal difficulty is an obvious time as well as cost advantage. Few interferences are noticed on the GC/MS system and the precision and accuracy of this technique indicate equivalency to a cryofocusing trap for air analysis as well as water analysis. A limited evaluation of the standards preparation procedure gives encouraging results for the utility of these techniques for an easy and inexpensive alternative for standard preparation.

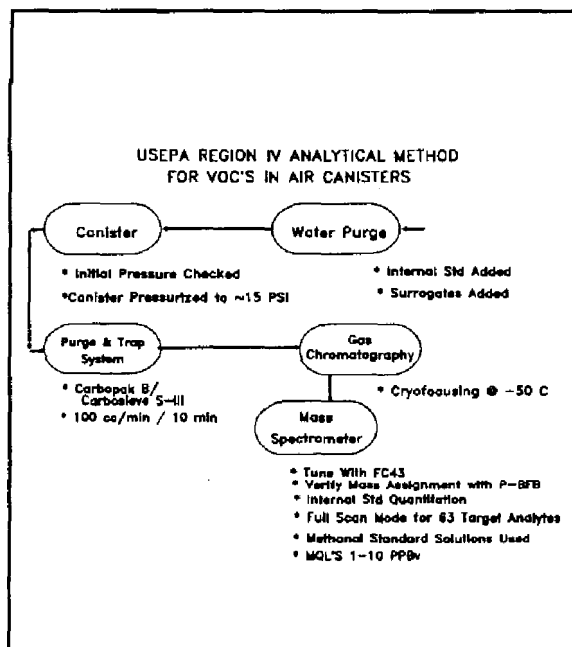


Figure 1

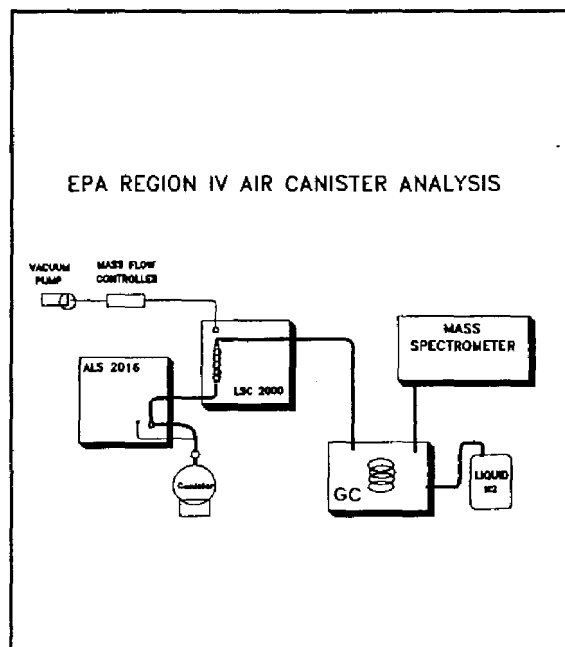


Figure 2

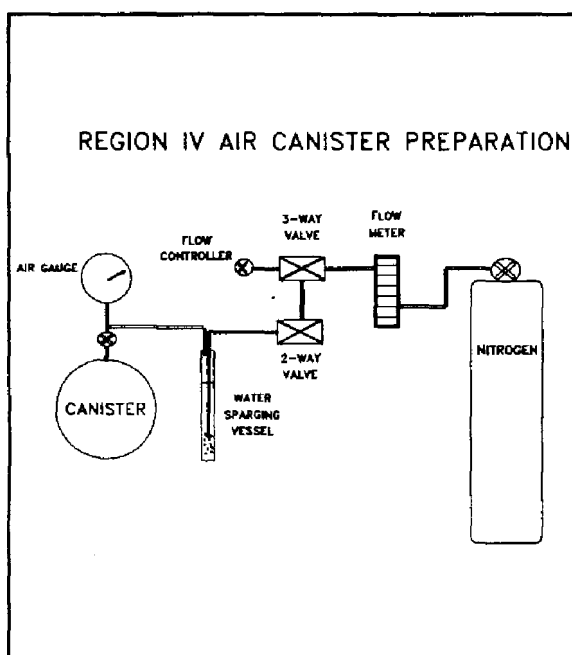


Figure 3

AUDIT CANISTER PREPARED 02-12-90 14:25
Equilibration Study

COMPOUND	TRUE VALUE	02-12 13:40 CONC PPBv	02-12 14:32 CONC PPBv	02-14 15:08 CONC PPBv
VINYL CHLORIDE	9.8	10.7	14.3	16
BROMOMETHANE	9.2	8.4	10.1	8.8
TRICHLOROFLUOROMETHANE	9.7	8.5	9.5	8.9
1,1-DICHLOROETHENE	9.4	8.4	8.8	9.1
METHYLENE CHLORIDE	8	4.8	5.5	6.4
1,1,2-DICHLOROETHANE	4.8	5.3	5.2	5.4
1,1-DICHLOROETHANE	9.5	11.8	11.8	9.3
METHYL ETHYL KETONE	1.6	7.0	3.7	4.8
CHLOROFORM	9.9	9.0	8.9	9.2
1,1,1-TRICHLOROETHANE	10.2	10.8	10.8	10.8
CARBON TETRACHLORIDE	10.5	9.4	8.4	8.7
BENZENE	9	4.5	4.4	4.5
TRICHLOROETHENE	10.2	9.0	8.8	9
1,2-DICHLOROPROPANE	8.2	4.2	4.2	4.5
TOLUENE	11.4	8.8	8.6	9.3
TETRACHLOROETHENE	10.6	7.8	7.3	7.8
CHLOROBENZENE	8.2	4.2	4.1	4.2
ETHYL BENZENE	5.8	4.5	4.4	4.5
O-XYLENE	5.8	4.0	3.8	3.8
STYRENE	2.2	1.8	1.0	1.7
1,1,2,2-TETRACHLOROETHANE		4.1	3.8	3.8

Figure 4

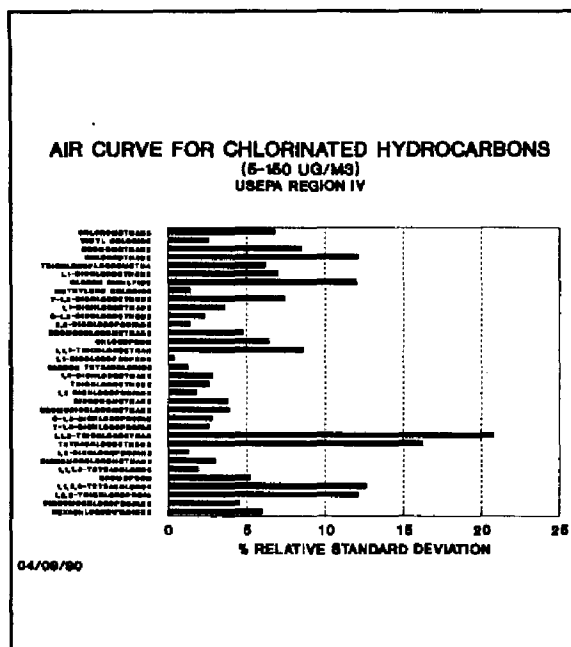


Figure 5

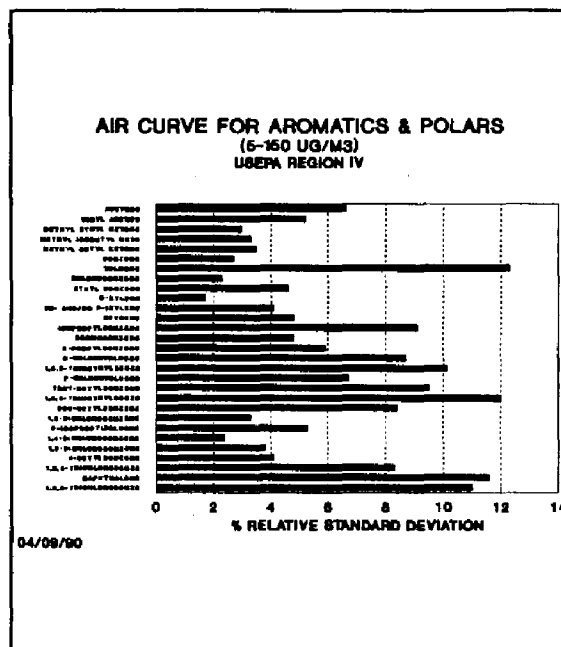


Figure 6

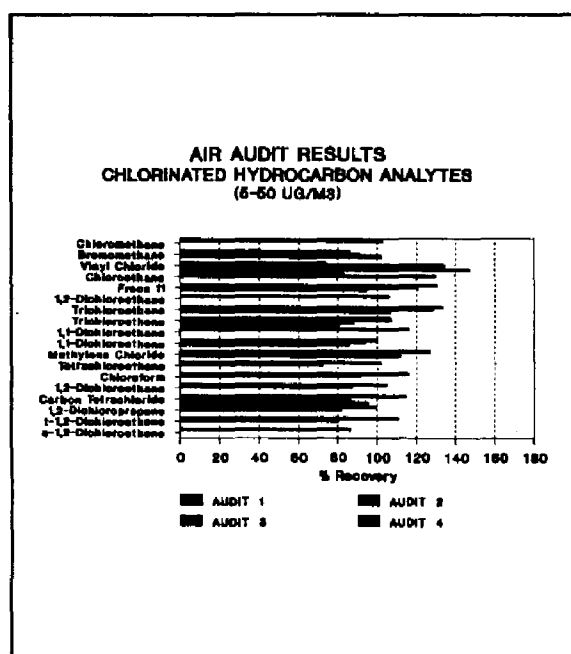


Figure 7

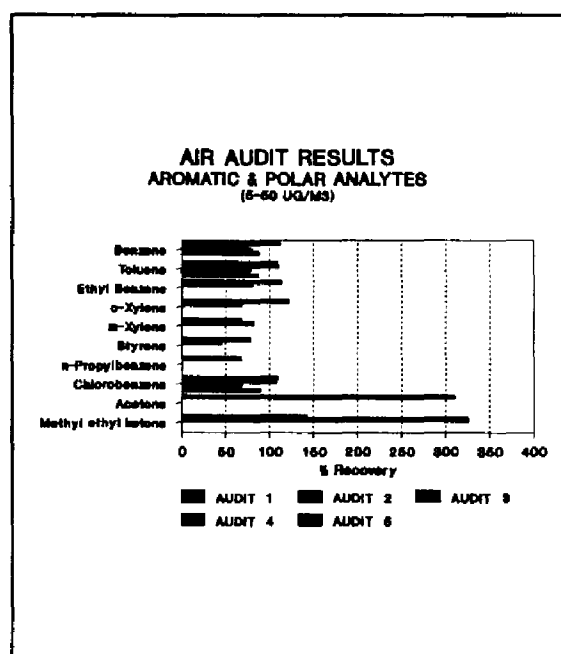


Figure 8

THE 1989 DELAWARE SITE STUDY

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Delaware Department of Natural Resources and Environmental Control

The Delaware SITE (Superfund Innovative Technology Evaluation) Study was carried out by a personnel from the Atmospheric Research and Exposure Assessment Laboratory (AREAL), U. S. EPA and AREAL contractors Battelle Columbus Laboratory, NSI Environmental Sciences and Tecan Remote, Incorporated. Personnel of the Delaware Department of Natural Resources and Environmental Control (DNREC) hosted the operation and obtained permission to use local sites for monitoring. The objective of the study was to field test several monitoring methods that have progressed through a feasibility testing stage and appear ready for predemonstration testing at Superfund sites. Monitoring occurred near four Superfund sites in the vicinity of New Castle, Delaware and at the Delaware Reclamation Plant located just north of the Delaware Memorial Bridge. Several different types of new monitoring equipment were deployed including: (1) automated gas chromatographs; (2) canister-based sequential samplers; (3) personal sampling devices; (4) canister-based sector samplers; (5) long path infrared transmission monitors; and (6) solid sorbent-based phenolic compound samplers.

Introduction

The Superfund Innovative Technology Evaluation (SITE) Program promotes the development, acceptance and use of promising innovative technologies capable of meeting the objectives of the overall Superfund Program. One objective of the program is to provide the means for developers of technology to demonstrate innovative technologies at Superfund sites as alternatives to the systems currently in use. A second objective is to provide support to stimulate the development of promising concepts and technologies to the point that they are suitable for demonstration at Superfund sites. In the case of the Delaware SITE program, a proposal was made by AREAL to the SITE program coordinator to carry out predemonstration testing of new monitoring techniques. After acceptance, a schedule was established for the testing in the summer of 1989.

The schedule of the SITE project consisted of the following items:

- Selection of a field site
- Predemonstration plan preparation
 - a. Planning/coordination meeting with participants; and
 - b. Preparation of plans for predemonstration testing.
 - 1. Documentation of experimental design; and
 - 2. Preparation and clearance of a quality assurance plan.
- Preliminary field screening study
- Preparation of a target compounds list for each test site
- Performance of the field testing
- Review of data and preparation of a highlight report
- Presentation of preliminary data at the 1990 EPA/AWMA Symposium on Measurement of Toxic and Related Air Pollutants
- Development of information products for the SITE program

The site proposed by J. J. Kliment of the Delaware Department of Natural Resources and Environmental Control (DNREC) was selected. The site was near New Castle, Delaware and included four Superfund sites and one site near the Delaware Reclamation Plant. A map of all the sites is shown in Figure I and detailed maps of all four sites are shown in the Figures II-IV. Figure I shows the Superfund sites: Army Creek, Delaware Sand and Gravel, Halby, and Standard Chlorine along with the Pigeon Point site which is near the Delaware Solid Waste Authority. The location of a monitoring site in the residential area referred to as Llangollen Estates and the P4 monitoring site maintained by the state of Delaware are also shown. The Standard Chlorine plant site was part of a large

industrial complex. Figure II shows some detail for the Army Creek, Delaware Sand and Gravel and the Llangollen Estates site. Figure III shows the industrial complex of which Standard Chlorine (location 12) is a part. Two state maintained monitoring sites marked S-20 and S-8 are shown on the map near Delaware City. Figure IV shows the Halby and Pigeon Point sites.

Experimental Plan

The experimental plan called for five methods of monitoring to be tested in the field. An automated gas chromatograph (GC) using a solid sorbant to preconcentrate volatile organic compounds (VOCs) from the ambient air was placed in the P4 station. The unit cycled through an automated sample and analysis sequence every hour. The objective for this monitoring method was to evaluate the use of a solid sorbant as a VOC preconcentrator and further to demonstrate the use of automated GCs as a means to establish the variability of VOC concentrations in time.

The P4 site was also used for placement of sector samplers. These units were placed at the P4 and S20 sites to characterize the industrial complex near Standard Chlorine. Data was also taken near the Army Creek and Delaware Sand and Gravel site using the sector samplers.

Personal sampling devices (PSDs) were used as fenceline dosimeters at several of the sites. These units sample by diffusion, are small and convenient to use. Since the units are less than two inches in diameter, they can be attached to any convenient structure and used to obtain a time-integrated ambient air sample. To establish the validity of the fenceline monitors for screening of VOCs, they were used in side-by-side tests with canisters.

Long path monitors based on selective absorption of infrared radiation by target gases, were used at four of the sites. The objective was to define the field capabilities of FTIR-based long path monitors. These monitors use source and receiver at one end of a monitoring path and a retro-reflector at the other end. The pathlength is typically 300 m long, giving a total pathlength of 600 m.

New solid sorbents specifically chosen for retention of phenolic compounds were also used at the Superfund sites. However, the field study was intended as a scoping study in this case since only laboratory studies had been done up to this point.

Screening Studies

A screening field study was performed at the Superfund sites in preparation for the main field study. Duplicate canister samples were taken at several locations simultaneously with the

operation of a Photovac Model 10S70 gas chromatograph. One canister was sent to each of two laboratories for analysis. Comparisons of the results of analysis have been given previously (1). Table I gives the results of a field screening analysis taken April 6, 1990, near a plant producing aromatic hydrocarbons. Other similar screening analyses at other sites gave significantly lower concentrations but were effective in characterizing the sites.

By using the results of screening analysis and the information obtained from emission inventories maintained by the state and from the SARA Title III disclosure statements, a target compound set was established for each site. Table II shows an example of a site specific target compound list. The field monitoring capabilities anticipated during the field study for the target compounds are indicated also.

Field Study

The main field study was carried out during the period 24 July through 9 August 1990 at the Superfund sites as planned. Individual experiments and experimental results were explained as part of the session on "The Delaware SITE Study" and are included in this Proceedings as the following six papers. One of the most interesting conclusions is that the dominant concentrations noted in monitoring close to "old" Superfund sites were due to local (within 5 km) industrial emissions.

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Disclaimer

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Table I. Site Specific Target Compound List

Site #1	Title III	Screen	Capability
Benzene	x	x	x
Chlorobenzene	x	x	x
<i>p</i> -Dichlorobenzene	x	x	x
<i>o</i> -Dichlorobenzene	x	x	x
<i>m</i> -Dichlorobenzene	x	x	x
Trichlorobenzene	x	x	x
Vinyl Chloride	x	x	x
Carbon Monoxide	x	-	x
Carbon Tetrachloride	-	x	x

Table II. SITE Screening Analysis+

Compound	ppbv	*	#
Benzene	4.5	x	x
Chlorobenzene	23.4	x	x
<i>p</i> -Dichlorobenzene	103.6	x	-
<i>o</i> -Dichlorobenzene	35.3	x	-
Trichlorobenzene	16.8	x	-

* Confirmed by Separate Analysis

Photovac Confirmation

+ 6 April 1989, near plant producing aromatic hydrocarbons

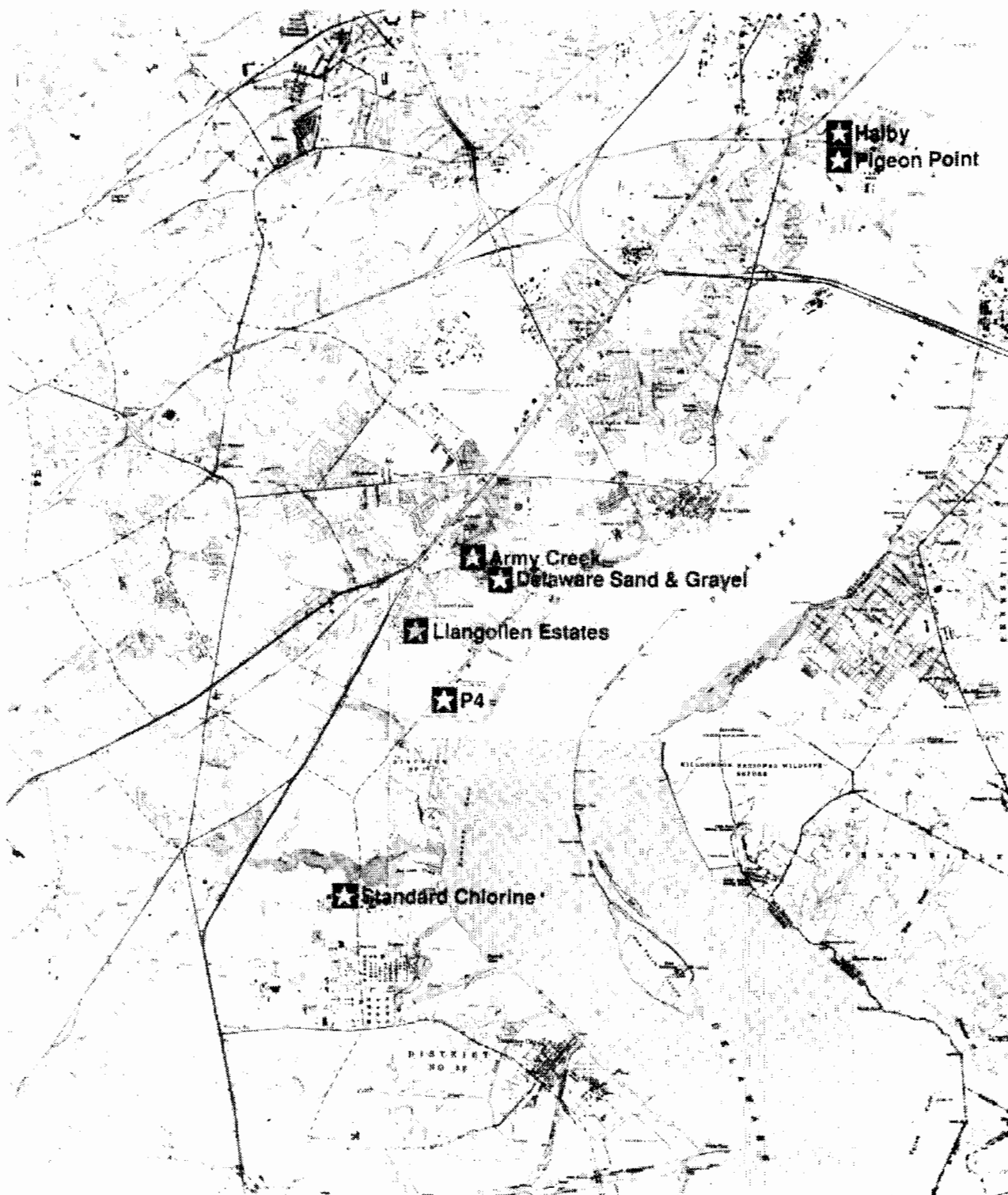
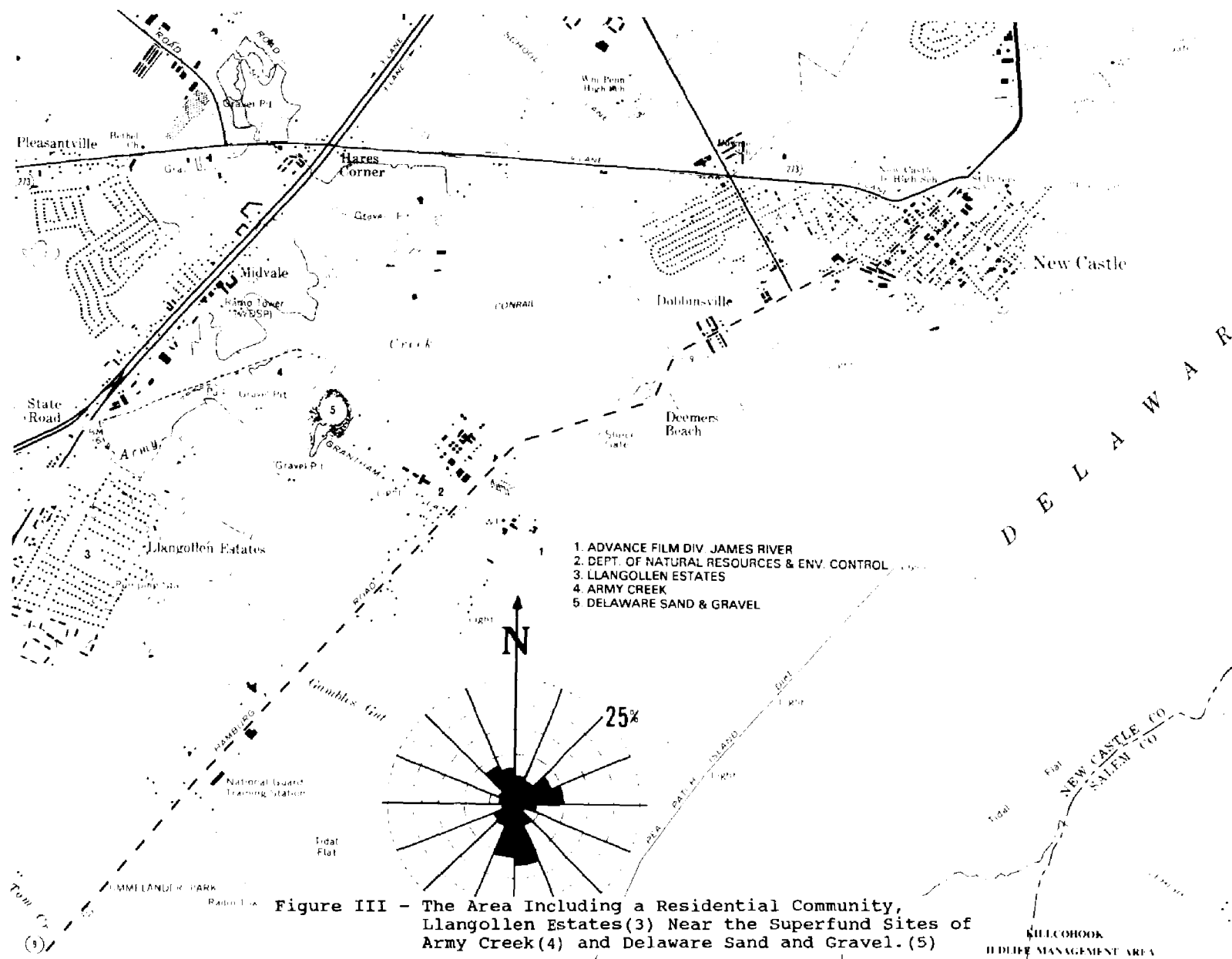
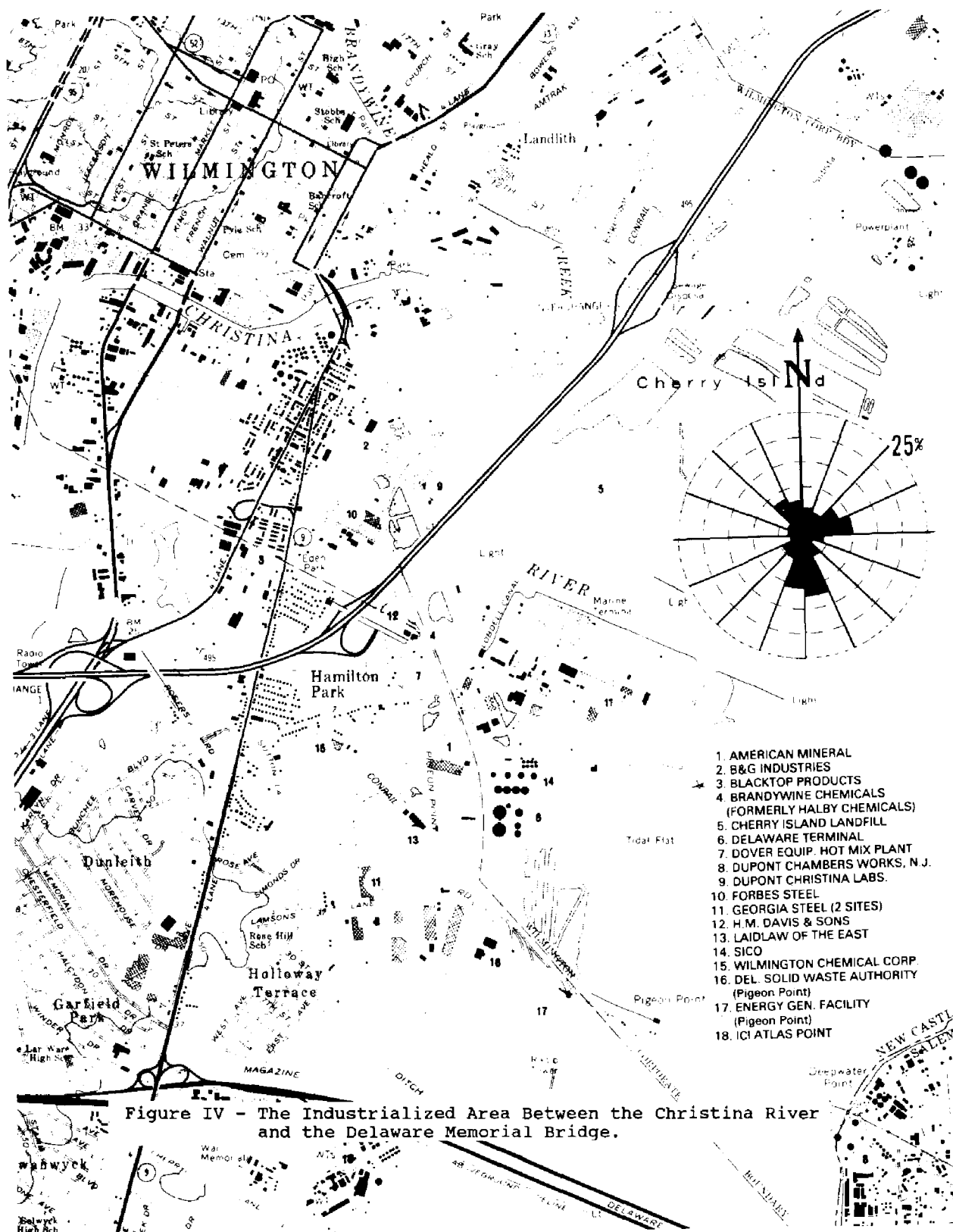


Figure I - Monitoring Sites for the 1989 Delaware SITE Study.

Figure II - The Industrialized Area Near Delaware City.





Multi-Adsorbent Preconcentration and Gas Chromatographic Analysis of Air Toxics with an Automated Collection/Analytical System

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Abstract

In order to identify and quantify the trace ppb levels of volatile organic compounds (VOCs) present in ambient air it is necessary to preconcentrate samples prior to analysis. Laboratory tests indicate that a collection trap containing several different adsorbents (multi-adsorbent trap) operating at ambient temperature, gave comparable sample collection capabilities as a glass bead trap that was cryogenically cooled. An automated gas chromatograph (GC) equipped with a multi-adsorbent trap was constructed and operated at a field site over a 12-day period to collect hourly samples of ambient air. Performance of the automated GC system was demonstrated by analyzing the data from daily calibration checks of the system using a 41-component VOC mixture at the 2 ppb level. Parallel flame ionization and electron capture detectors were used to detect these components. Relative standard deviation values of less than 10 percent were obtained for most of the 41 compounds. No downtime was experienced with the instrument, and operator interface was limited to performing daily calibration checks, transferring data to floppy disks, and replacing gas supplies.

Introduction

Many of the volatile organic compounds (VOCs) found in ambient air are present at very low parts per billion (ppb) and parts per trillion (ppt) levels. In order to identify and quantify these species, researchers must employ collection techniques that preconcentrate sufficient amounts of these materials for analytical detection.

The use of cryogenic trapping to concentrate VOCs prior to analysis has been established as a proven technique for VOC monitoring (1-5). This method involves collecting the sample on an inert material at subambient temperatures. The temperature of the trap is below the condensation temperatures for trace VOCs but above the condensation temperature for major constituents of ambient air. After collection the trap is rapidly heated, and the VOCs are desorbed and typically analyzed using a gas chromatographic (GC) system. For optimal analytical resolution, the GC oven is also cryogenically cooled. This allows the desorbed VOCs to be refocused onto the front of the column as a tight band prior to temperature programming.

The use of cryogen has proven to be not only a costly consumable but also a logistic problem when monitoring air toxics during field sampling studies. An alternative to cryogenic trapping is the use of adsorbent materials, which collect VOCs at ambient temperatures. Popular adsorbents include Tenax-TA, silica gel, carbon molecular sieves, and activated charcoal. Desorption again is accomplished by elevating the trap temperature prior to GC analysis. A deficiency associated with mono-adsorbent traps is their inability to trap and/or desorb VOCs possessing a wide range of molecular weights (6,7).

The purpose of this paper is to: (1) describe a multi-adsorbent trapping system designed for the automated collection and analysis of ambient air samples; (2) compare the efficiency of trapping a variety of VOCs using a

multi-adsorbent trap versus a cryogenic assembly; and (3) discuss results from a 12-day ambient air sampling field study using a multi-adsorbent system.

Experimental Section

Analytical Instrumentation

The gas chromatographic system that was assembled for the automated collection and analysis of ambient air samples consists of a Hewlett Packard 5890A GC equipped with a flame ionization detector (FID) and an electron capture detector (ECD). Hewlett Packard 3396A and 3393A integrators in conjunction with a 9122 disk drive receives detector output signals and stores data. The disk drive also provides access to the BASIC program used to automate sample collection and analysis.

Separations chemistry is accomplished using two 30-meter, HP-1 series, capillary columns joined with a zero dead-volume, butt connector. Internal diameter (ID) of the capillary is 0.53 mm with a 2.65 μm film thickness. The end of the capillary column is fitted with a zero dead-volume tee. Lengths of 0.32 mm ID, deactivated, fused-silica (≈ 25 cm for ECD, ≈ 40 cm for FID) are used to direct about 30% of the column effluent to the ECD while $\approx 70\%$ goes to the FID. Optimal analytical separation is obtained using a temperature program of -50°C to 200°C with an initial hold of 2 minutes and ramp of $8^{\circ}\text{C}/\text{minute}$. Zero-grade helium with a flow rate of $7.5\text{ cm}^3/\text{minute}$ constitutes the carrier gas. FID gases are ultra zero-air ($300\text{ cm}^3/\text{minute}$) and zero hydrogen ($30\text{ cm}^3/\text{minute}$). Zero nitrogen, ($40\text{ cm}^3/\text{minute}$) passes through an Alltech Oxy-Trap (Cat. No. 4003), and serves as makeup gas for the ECD.

Sample Collector

A modified Nutech 320 sample preconcentration unit is used to collect ambient air. The unit contains two subsystems: (1) an electronics console that regulates various temperature zones and (2) the sample handling subassembly containing a six-port valve and the trap assembly (Figure 1). The console controls the temperatures of the valve body (120°C), sample transfer lines (120°C), and the trap. The trap temperature during sample collection is regulated by the console with the controlled release of liquid nitrogen via a solenoid valve. Set-points are -150°C during collection for the glass bead trap and 40°C for the multi-adsorbent trap. During thermal desorption, the glass bead trap is heated by a 250 watt heater to 90°C . The same type of heater is used to desorb the multi-adsorbent trap at 220°C . A Valco, Model A602, air actuator drives the six-port valve from the sample collection to sample injection positions. The entire sample handling subassembly is mounted onto the HP5890A GC where the injectors would normally be located. The connection between the valve and analytical column is made using a stainless steel union with graphite vespel ferrules.

Trap Design and Sample Collection

The trap assembly is shown in Figure 2. The trap consists of 0.2-cm ID stainless steel tubing coiled around the desorption heater. The cryogenic trap is packed with 0.20 gram of glass beads (60/80 mesh). The multi-adsorbent trap, which was purchased from Supelco, Inc. (Cat. No. 2-0321), contains 0.20 gram of Carbopack B (60/80 mesh) and 0.05 gram of Carbosieve S-III (60/80 mesh). This type of trap is used to perform U.S. EPA Methods 624 and 824 which address the collection and analysis of VOCs from water by purge and trap. The Supelco trap is cut to length and wound around a 1.8-cm o.d. stock prior to being coiled onto the heater.

Sample flow through the trap is controlled using: (1) a Tylan readout control unit, Model R032-B; (2) a Tylan 0 to 100 standard cubic centimeters per minute mass flow controller, Model MFC-260; (3) a Thomas dual diaphragm pump; and (4) a Perma Pure Dryer, Model MD-125-48F. The readout control unit in conjunction with the mass flow controller regulates air flow rate through a sampling manifold into the trap. Typically, the sample flow rate is 35 cm³/minute with a collection time of 10 minutes. The perma pure dryer with a tubular hygroscopic ion-exchange membrane (Nafion) is used to remove water vapor selectively from the sampled gas and is placed upstream of the trap. The tube size is 30 cm x 0.1 cm ID, embedded within a shell of Teflon tubing of 0.25 cm ID. A countercurrent flow of dry zero air (200 to 300 cm³/minute) is used to purge the shell. The use of this type of dryer has been shown to have no affinity for the VOCs of interest in this study (4,5,8). The multi-adsorbent trap is installed in a manner that allows sample flow initially through the Carbopack B material and then onto the Carbosieve S-III. During desorption, the trapped VOCs are backflushed off of the trap. The sample flow scheme is shown in Figure 3.

Automated Sampling and Analysis

A BASIC program permits automated sampling and analysis procedures to be carried out. A run is initiated by activating the program using the HP-3396A integrator via the INET loop connecting the GC and the 9122 disk drive. When the program starts, five prompts are presented that require an input from the analyst. These include the number of samples to run, run name, trap collection time, trap cool down time, and clock start run time. Details of the BASIC program are presented elsewhere (10).

Gas Standard Used In Evaluating GC System

The gas chromatographic system is calibrated by injecting measured amounts of a diluted mixture from a calibration cylinder. A gas phase dynamic dilution system is used to generate nominal concentrations of 2 to 4 ppb of each of these target compounds. Zero air (Aadco, Inc.) serves as the diluent.

The target compounds were obtained as gases or neat liquids (>98 % purity) from Matheson, Eastman Kodak, Baker Chemical, or Aldrich Chemical Company. A compressed gas cylinder mixture of the compounds is prepared by injecting predetermined amounts of each test compound into an aluminum cylinder that has been flushed with high-purity nitrogen gas and evacuated. After injection of the gas or neat liquid, the cylinder is pressurized to 1,200 psig with zero air. In order to verify component concentrations, an accurately measured quantity of each of the compounds is injected into a 17.3 m³, Teflon-lined, aluminum chamber. After equilibration, a GC response factor is determined for each compound by withdrawing a known volume of air from the chamber and injecting it into the gas chromatographic system. This same procedure is used to analyze the gas cylinder standard. Concentrations are calculated using the derived response factors. For the above compounds, the calculated cylinder concentrations are within $\pm 20\%$ of the 200 ppbv nominal targeted values.

Trap Evaluation

A glass bead trap was initially installed into the trap/valve subassembly. A humidified 41-component standard mixture (2 to 4 ppb) was directed into a clean 6-liter, Summa polished, stainless steel sampling canister and the trapping/analysis system was challenged with this calibration standard. Evaluation of instrument performance was made by comparing

qualitative/quantitative results for the newly constructed unit with analytical results obtained using a reference gas chromatographic system equipped with parallel flame ionization and mass selective detectors. The glass bead trap/full cryogenic reference GC system has a record of excellent performance based on audit analysis on previous studies carried out at Battelle (9). Once it was shown that comparable results are being obtained on both systems, then the multi-adsorbent trap was challenged with the same 41-component mixture. Performance of the multi-adsorbent system was based upon comparing target compound recoveries with those observed for the cryogenic, glass bead system.

Field Test of Automated System

The automated GC system, with the multi-adsorbent trap as the whole air concentrating device, was subjected to a 12-day field test. During this time the system ran continuously for 10 days collecting and analyzing whole air samples on an hourly basis. The only interruption in the sampling regime occurred when a daily performance check was made using the 41-component calibration mixture. The analytical conditions were the same as those already mentioned in this paper.

Results and Discussion

Comparison of Cryogenic to Multi-Adsorbent Trapping

Tables I and II show the results comparing the relative performance of the multi-adsorbent trap to the cryogenic trap. The FID results show excellent agreement between the two traps for most of the compounds. The species displaying lower than expected recoveries are in general compounds with poor FID response (peaks 1 through 7 in Table I). Because of this poor response, typically both the cryogenic and multi-adsorbent traps displayed large relative standard deviation (RSD) values. These compounds did respond well to the ECD and the RSD values reflect acceptable recoveries as shown in Table II.

Six test runs were made that involved the side by side comparison of two similar GC systems, one equipped with a cryogenic trap and the other with the multi-adsorbent trap discussed in this paper. These analyses of ambient air showed that most of the FID and ECD responding compounds for the two GC systems were within ± 25 percent of the mean concentration (10).

Field Study

Due to the favorable comparison of the multi-adsorbent trapping system to a full cryogenic unit, the adsorbent system was utilized in a field study. Field data results are reported elsewhere (11). However, several results that further demonstrated trapping efficiencies and instrument performance are reported here.

During the field study a single point calibration check was performed daily. The results are shown in Table III. The RSDs were derived from the raw peak areas observed over the 12-day period. The data indicate excellent precision for most of the 41 components. Compounds that respond to both the FID and ECD have both RSD values reported. Differences in these values generally reflect individual response characteristics of those compounds to the specific detector. The one compound that did show poor RSD values on both detectors was dichlorodifluoromethane. This result agrees with earlier laboratory data shown in Tables I and II.

On the final day of the field sampling program, the room environment that housed the GC system during the study was sampled. Immediately after that analysis, a sample of zero air (Airco) was collected and processed through the GC system. The room air was indicative of the types and concentrations of compounds found during the study. Several of the predominant peaks are identified. In reviewing the chromatogram of the zero air, it is apparent that no carryover occurred from the previous sample collection. The only apparent artifact peak from the multi-adsorbent trap occurred at 24.2 minutes and is observed in both analyses. Based upon an equal carbon atom response by the FID, this peak corresponds to a concentration of 0.2 ppb carbon.

Concurrent with the evaluation of the trap was the assessment of the automated sample collection/analytical hardware. During the study the system performed uninterrupted analyses with minimal operator interaction. The hourly ambient air sampling was halted to perform the daily calibration run and change any consumables such as chart paper or gases, but these were the only times the instrument was not online monitoring the status of the air at the site. No downtime repairs were required.

The field GC system employed liquid nitrogen to cool the analytical column and thereby enhance peak resolution. Prior to the field study, efforts were made to either eliminate or reduce the consumption of cryogen without sacrificing peak resolution. Various types of capillary columns and a prototype cryo refocusing device were evaluated, and these results are reported elsewhere (10). We used the adsorbent trap instead of the cryogenic glass bead trap yet still utilized liquid nitrogen to cool the analytical column. In this configuration a 30% reduction of liquid nitrogen consumption was realized. Another advantage in using the adsorbent trap is that extended collection times do not result in greater cryogen consumption as would be the case with glass bead trapping.

In the current configuration, the system is sampling the air for 10 minutes every hour. Potentially, this could result in the loss of detecting a discrete plume moving across the site. The flexibility inherent with this analytical system makes it possible to modify the BASIC program to allow extended collection coverage. Up to 79% sampling time coverage of the monitoring cycle is possible using a single system by overlapping sample collection for the next run while the analysis of the previous collection is being performed (4).

Trap/Valve Subassembly Modification

The evaluation of adsorbent traps brought about a modification to previously constructed air sampling units. The trap/valve subassembly shown in Figure 1 allows for the rapid installation and removal of different traps. Earlier designs demanded several hours of effort to change traps (4,5). The new configuration has converted the trap/valve into two separable parts: one contains the valve/actuator, while the other contains the trap/heater. The trap/heater attaches to the rest of the assembly with Swagelock and electrical quick-connect fittings. This modification allows for the removal of the existing trap assembly and installation of another complete trap/heater unit within 20 minutes. As a result, it is possible to change traps rapidly to meet new analytical needs or to replace a defective unit.

The use of a multi-adsorbent trap has resulted in a system that is more versatile and less costly to operate than other units without sacrificing analytical performance.

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Table I. Performance of the multi-adsorbent trap compared with the cryogenic trap (3-runs), using flame ionization detector response.

Compound	Concentration (ppb)				
	Cryogenic	% R.S.D.	Multi-Adsorbent	% R.S.D.	% Recovery
1) dichlorodifluoromethane	2.88	8.18	8.91	78.77	35
2) methyl chloride	2.84	15.17	3.25	28.99	123
3) 1,2-dichloro-1,1,2,2-tetrafluoroethane	2.88	*	**	**	**
4) vinyl chloride	4.81	17.83	3.92	1.68	85
5) methyl bromide	3.88	7.49	2.18	9.81	71
6) ethyl chloride	2.58	6.38	2.23	3.49	88
7) trichlorofluoromethane	2.74	84.28	1.45	47.84	53
8) 1,1-dichloroethene	3.22	8.25	3.12	3.82	97
9) dichloromethane	4.11	7.19	3.98	5.42	96
10) 3-chloropropene	3.22	3.34	3.13	2.21	97
11) 1,1,2-trichloro-1,2,2-trifluoroethane	2.72	5.25	2.82	8.89	98
12) 1,1-dichloroethane	3.87	12.39	2.78	5.41	91
13) cis-1,2-dichloroethene	3.48	2.38	3.52	3.58	181
14) trichloromethane	3.45	7.29	3.48	9.98	181
15) 1,2-dichloroethane	3.34	2.52	3.33	1.67	188
16) 1,1,1-trichloroethane	2.88	3.48	2.58	6.39	97
17) benzene	2.83	8.97	2.98	1.58	185
18) carbon tetrachloride	2.98	8.27	3.18	3.83	187
19) 1,2-dichloropropane	2.89	2.13	2.88	1.48	99
20) trichloroethene	2.93	2.38	3.22	3.82	118
21) cis-1,3-dichloropropene	2.93	1.46	2.82	5.89	98
22) trans-1,3-dichloropropene	2.93	3.24	2.81	1.72	89
23) 1,1,2-trichloroethane	2.83	2.18	2.81	1.31	99
24) toluene	2.45	2.45	2.51	3.13	182
25) 1,2-dibromoethane	3.88	6.75	2.98	4.71	95
26) tetrachloroethene	2.51	7.51	2.47	4.98	98
27) chlorobenzene	2.54	5.42	2.58	2.35	182
28) ethylbenzene	2.18	5.31	2.19	1.48	181
29) m+p-xylene	2.14	5.88	2.21	4.21	183
30) styrene	2.25	6.51	2.18	1.87	98
31) 1,1,2,2-tetrachloroethane and o-xylene	4.37	3.52	4.29	1.87	98
33) 4-ethyltoluene	1.83	5.97	1.85	1.87	181
34) 1,3,5-trimethylbenzene	1.83	4.98	1.88	2.12	98
35) 1,2,4-trimethylbenzene	1.88	6.19	2.87	18.47	118
36) benzyl chloride and m-dichlorobenzene	4.28	8.58	3.92	3.29	93
38) p-dichlorobenzene	1.78	4.37	1.79	1.78	181
39) o-dichlorobenzene	2.18	5.88	2.19	2.94	181
40) 1,2,4-trichlorobenzene	1.64	18.88	1.57	12.33	98
41) hexachlorobutadiene	1.37	9.78	1.24	8.57	91

* = only one data point.

** = no data.

Table II. Performance of the multi-adsorbent trap compared with the cryogenic trap (3-runs), using the electron capture detector response.

Compound	Concentration (ppb)				
	Cryogenic	% R.S.D.	Multi- Adsorbent	% R.S.D.	% Recovery
1) dichlorodifluoromethane	2.68	4.09	2.90	1.03	112
2) 1,2-dichloro-1,1,2,2-tetrafluoroethane	2.68	5.73	2.81	0.24	105
3) methyl bromide	3.06	11.35	2.88	1.44	88
4) trichlorofluoromethane	2.74	1.33	2.79	0.27	102
5) 1,1,2-trichloro-1,2,2-trifluoroethane	2.72	0.07	2.71	0.20	100
6) trichloromethane	3.45	0.74	3.45	0.11	100
7) 1,1,1-trichloroethane	2.68	0.32	2.60	0.25	98
8) carbon tetrachloride	2.96	0.49	2.92	0.12	99
9) trichloroethene	2.93	0.54	3.22	0.42	110
10) 1,2-dibromethane	3.06	1.45	2.93	0.45	96
11) tetrachloroethene	2.51	0.92	2.53	0.03	101
12) 1,1,2,2-tetrachloroethane	2.23	3.01	1.99	0.38	89
13) m-dichlorobenzene	2.16	**	2.30	3.24	107
14) p-dichlorobenzene	1.78	**	1.63	2.89	108
15) o-dichlorobenzene	2.16	6.76	2.29	1.66	106
16) 1,2,4-trichlorobenzene	1.84	**	1.82	6.10	111
17) hexachlorobutadiene	1.37	8.16	1.28	0.03	93

** = only single run used.

Table III. Analytical precision of multi-adsorbent GC system during field study (12 runs).

Compound	Challenge Concentration (ppb)	FID % R.S.D.	ECD % R.S.D.
1) dichlorodifluoromethane	2.68	*	98.1
2) methyl chloride	2.64	9.63	**
3) 1,2-dichloro-1,1,2,2-tetrafluoroethane	2.68	53.8	4.23
4) vinyl chloride	4.81	1.37	**
5) methyl bromide	3.88	3.61	18.6
6) ethyl chloride	2.58	3.98	**
7) trichlorofluoromethane	2.74	142	2.18
8) 1,1-dichloroethene	3.22	3.11	**
9) dichloromethane	4.11	7.41	**
10) 3-chloropropene	3.22	3.77	**
11) 1,1,2-trichloro-1,2,2-trifluoroethane	2.72	3.92	1.98
12) 1,1-dichloroethane	3.87	1.34	**
13) cis-1,2-dichloroethene	3.48	2.82	**
14) trichloromethane	3.46	1.85	8.82
15) 1,2-dichloroethane	3.34	1.84	**
16) 1,1,1-trichloroethane	2.66	8.98	9.96
17) benzene	2.83	2.28	**
18) carbon tetrachloride	2.96	1.88	7.79
19) 1,2-dichloropropane	2.89	1.68	**
20) trichloroethene	2.93	1.47	2.48
21) cis-1,3-dichloropropene	2.93	1.78	**
22) trans-1,3-dichloropropene	2.93	2.13	**
23) 1,1,2-trichloroethane	2.83	1.28	**
24) toluene	2.45	1.62	**
25) 1,2-dibromoethane	3.88	1.48	11.1
26) tetrachloroethene	2.51	2.13	2.82
27) chlorobenzene	2.54	1.42	**
28) ethylbenzene	2.18	1.52	**
29) m+p-xylene	2.14	1.35	**
30) styrene	2.25	4.18	**
31) 1,1,2,2-tetrachloroethane and o-xylene	4.37	1.41	3.14
33) 4-ethyltoluene	1.83	1.33	**
34) 1,3,5-trimethylbenzene	1.83	1.71	**
35) 1,2,4-trimethylbenzene	1.88	2.48	**
36) benzyl chloride and m-dichlorobenzene	4.28	2.87	8.46
38) p-dichlorobenzene	1.78	3.78	8.88
39) o-dichlorobenzene	2.18	1.72	7.19
40) 1,2,4-trichlorobenzene	1.64	1.53	18.8
41) hexachlorobutadiene	1.37	3.91	4.38

* = not detected.

** = does not respond.

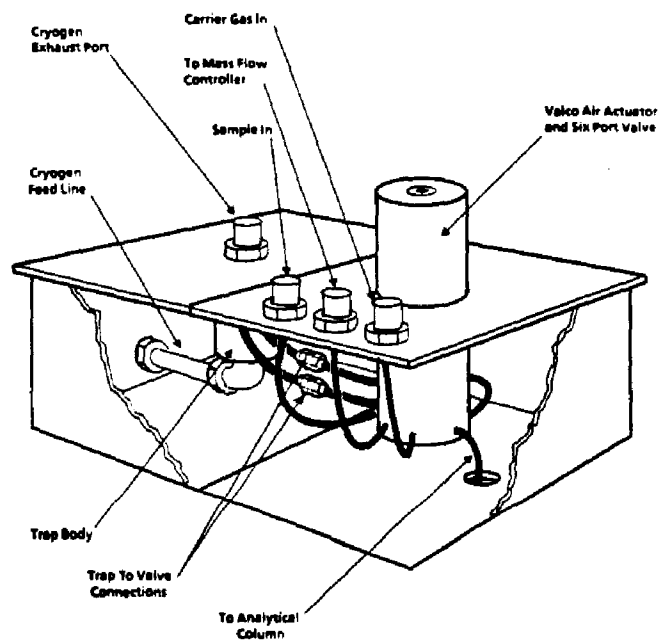


Figure 1. Trap/valve subassembly.

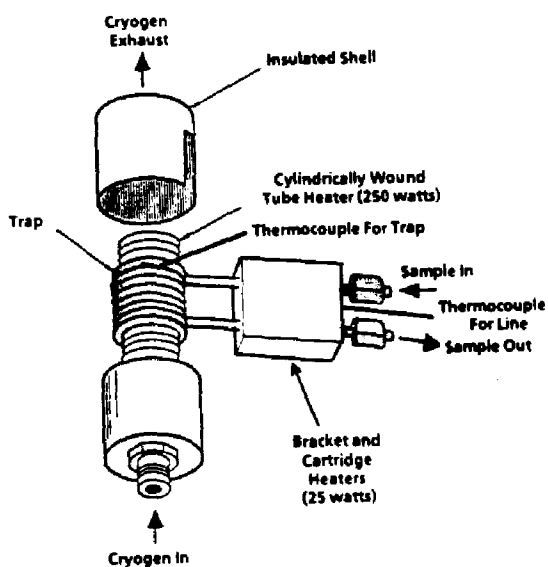


Figure 2. Trap assembly.

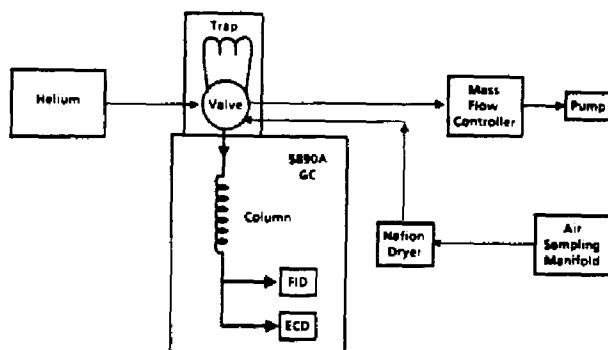


Figure 3. Sample flow scheme for the automated system.

**PASSIVE SAMPLING DEVICES AND CANISTERS: THEIR COMPARISON IN
MEASURING AIR TOXICS DURING A FIELD STUDY**

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With wide usage of passivated canisters in ambient air sampling, any acceptance of an alternate or supplemental sampling technique would first require a favorable comparison with canister samplings under identical field conditions. A reusable passive sampling device (PSD) that contains a thermally desorbable sorbent, such as Tenax-GC®, potentially offers the advantages of unobtrusive sampling, rapid recycling, and simplified operation. For laboratory comparisons, canisters and PSDs simultaneously sampled ambient air containing air toxics (>40 VOCs) that are measured by the gas chromatographic TO-14 Method. In this case, a prototype PSD thermal desorber was added to the GC system; the cryogenic trapping and chromatographic detection (FID; ECD) were common paths for the VOCs from pressurized canisters or desorbed PSDs. Field comparisons were warranted after GC backgrounds from desorbed PSDs were minimized by (1) thermal bulk cleaning under vacuum and (2) improving the individual PSD storage units. In August, 1989, 11 sampling events (1 canister with 2 PSDs/event) were taken at 4 sites during a Superfund Innovative Technology Evaluation (SITE) Study in Delaware. Large concentration differences between sites were measured for benzene, toluene, chlorobenzene, and *p*-, *m*- and *o*-dichlorobenzene; comparative data indicate this PSD method could also accurately screen these sites for these VOCs. This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

INTRODUCTION

There is continued interest in passive sampling devices (PSD) because they appear to satisfy the growing need for more simple, inexpensive methods to sample the low levels of volatile toxics in ambient air. In many cases, a large data base, resulting from a large number of samples taken, is required before environmental problems can be clearly understood.

Although chemical alterations can occur during thermal desorption from sorbents such as TenaxGC®, there is at least a 200-fold greater sensitivity to be gained by analysis of the total desorbed sample, an advantage that is lost with solvent-extracted PSDs. However, the PSD exposure time versus the retention volume for a desired chemical species will often limit any ambitions for a single sorbent to possess wide-spread, quantitative applications. For these reasons, the selection of PSDs for preliminary initial screenings of unknown environments may need to be based upon detecting different chemical classes.

The objective of this paper was to compare canister and PSD data under field conditions. In this instance, the utility of the PSD was enhanced by limiting its detection to an aromatic class of chemicals (substituted benzenes) that demonstrated large retention volumes for the sorbent.

EXPERIMENTAL

Selection of Sampling Sites and VOCs

Canister grab samples were taken from clustered sites near or within New Castle County, Delaware and analyzed for volatile organic toxics (Method TO-14). Based on these data, the following four sites were selected for PSD/canister intercomparison: a superfund site (Site A); a landfill (Site B); a state monitoring station (Site C); and an active industrial complex (Site D). The described PSD/canister comparisons at these sites were part of the Superfund Innovative Technology Evaluation (SITE) Program.

Benzene, toluene, chlorobenzene, and *p*-, *m*- and *o*-dichlorobenzene were the VOCs selected for this comparison. These aromatics were verified by GC-MS in the initial site screenings and favorable, high retention volumes for these VOCs were demonstrated in the TenaxGC®-PSD used (1).

Instrumentation

A Hewlett-Packard 5880 gas chromatograph, equipped with flame ionization and electron capture detectors and fitted with a cryogenic trap for concentrating VOCs (2), was connected to a prototype PSD desorber fabricated by Nutech, Inc. As shown in Figure 1, VOCs from either a canister sample (left side) or a thermally desorbed

PSD (right side) share a common cryogenic trap (-150C) for pre-concentration prior to chromatographic analysis (HP-1 0.53 mm ID X 30 m capillary column, 0.88 micron thickness; -50 to 150C thermal program). Multi-level calibration was performed to accommodate the wide range of VOC concentrations sampled at the selected sites.

PSD Analysis

Passive sampling devices (PSDs), each containing 0.4 g Tenax-GC® with experimentally measured VOC sampling rates for the reported VOCs were bulk cleaned in a stainless steel, teflon o-ring sealed cylinder at 110C under 20 micron vacuum for 8 hours. The hot evacuated cylinder was brought to atmospheric pressure by adding nitrogen gas. After cooling, the PSDs were transferred to their individual air-tight containers under a nitrogen atmosphere and then stored in nitrogen-purged metal cans until exposed. Previous tests indicated this bulk cleaning procedure would provide a consistent ECD/FID background between PSDs for the duration of the field study and subsequent period for analysis. After a PSD was thermally desorbed 10 min in a sealed chamber (Figure 1, far right) at 180C, the desorbed VOCs were transferred and recollected into a -150C cryotrap (Figure 1, far left) by purging the heated chamber with a 30 cc/min Helium flow for 10 min.

Canister Analysis

Six L canisters were subjected to three cycles of evacuation and pressurization with ultra-pure air prior to final evacuation to 20 microns. Random analyses of the cleaned canisters were performed prior to the field study. After collection of field samples, the canisters were pressurized to 20 psig and the VOCs from a 300 cc atmospheric aliquot were trapped in the -150C cryotrap at 30 cc/min prior to chromatographic analysis.

Field Sampling

A sampling event was represented by a two hour cocollection of a single canister with paired PSDs; 11 sampling events were taken over a four day period between 9:00 and 15:30. Days were either overcast or sunny during the sampling period; no rainfall occurred. Canisters were fitted with a linearized sampling orifice that provided a constant 25 cc/min sampling over the 2 hour sampling. Readings of residual vacuum in the canisters after sampling were immediately recorded and these values rechecked prior to analysis. Three random PSDs remained unopened as controls during sampling and provided a background average for the sampled PSDs. The exposed PSDs were placed within 10 cm of the canister sampling orifice and a metal roof protected all sampling events.

RESULTS AND DISCUSSION

Eight of the 11 sampling events (11 canisters and 25 PSDs) collected during this study were taken at Sites A, B and C and the analytical data for six volatile organics during the eight events are presented in Table I. The superfund site, the landfill and the state monitoring station provided similar VOC levels that did not exceed 10 ppbv. The screening ability of the PSDs is indicated by the general agreement to measured canister concentrations. Assessments of benzene, toluene and chlorobenzene exposure could be performed using either canister or PSD samples; however, the PSD consistently provided information on the dichlorobenzenes that was not always obtained by canister analysis. This was to be expected at sub-ppbv detection levels because the exposed PSD represented a 10-fold sampling volume to that used in the canister analysis.

Figure 2 graphically compares PSD and canister data from three sampling events at an industrial complex having high VOC concentrations (5 to 293 ppbv range). The PSDs indicated a general agreement with the corresponding canister concentrations and they show promise as a screening tool for locating pollutant sources, especially when the preselected aromatics have large retention volumes for the sorbent (1,3). Viewing the general close agreement from the paired PSDs, it not understood why the *p*-chlorobenzene data from the first two events showed a wide spread; however, it can be seen that the PSD averages were similar to the concomitant canister data. From a verbal report (4) that described the rapid VOC fluctuation during long path measurements made at Site D during this same period, it is not clear that errors in PSD sampling occurred.

CONCLUSIONS:

In this field study, the passive sampling devices agreed with respective canister data in assessing the targeted aromatic volatile concentrations at four sampling sites. If only PSDs were chosen as site screening devices, the following sampling recommendations are as follows:

1. Several progressive exposure periods (30 -120 min) should be used, especially if the targeted VOCs have marginal retention volumes. A three PSD/site minimum should be taken since analysis of sample aliquots is not currently possible.
2. In general, agreement between canister and PSD concentrations appeared concurrent with close toluene results; therefore, toluene levels between TenaxGC®-PSDs should be compared in assessing sample integrity.

3. The prototype PSD desorber-GC system produced chromatography equal to that achieved with canister sampling. It is recommended that both flame ionization (FID) and electron capture detectors be used when a wide range of concentrations may be encountered.

DISCLAIMER

The research described in this article does not necessarily reflect the views of the Agency and no official endorsement should be inferred. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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TABLE 1. Comparison of PSD and canister air sampling at three sites in Delaware Field Study. Superfund Site (A); Landfill (B); State Monitor Station (C).

Sampling Events:	SITE A			SITE B			SITE C	
	1	2	3	4	5	6	7	8
<u>Analyte:</u>								
Benzene:								
PSD #1	1.20	0.80	0.28	2.75	2.97	0.86	3.15	2.48
PSD #2	1.30	---- ^a	0.44	1.64	2.12	1.20	3.14	2.39
PSD avg	1.25	0.80	0.36	2.19	2.54	1.03	3.15	2.44
Canister	3.75	1.18	0.92	2.11	2.33	0.32	2.35	2.33
Toluene:								
PSD #1	6.26	1.60	0.95	7.63	7.34	2.57	8.60	9.57
PSD #2	7.50	----	1.18	4.91	4.18	3.28	9.32	9.39
PSD avg	6.88	1.60	1.06	6.27	5.76	2.93	8.96	9.48
Canister	5.32	2.17	1.88	5.54	3.97	1.15	6.05	5.37
Chloro- Benzene:								
PSD #1	2.14	0.75	1.76	1.36	0.68	2.54	3.77	0.22
PSD #2	2.90	----	2.46	2.42	3.36	2.49	3.72	0.23
PSD avg	2.52	0.75	2.11	1.89	2.02	2.52	3.75	0.23
Canister	2.05	1.41	1.05	1.02	0.96	2.03	1.12	0.78
m-Cl₂- Benzene:								
PSD #1	0.65	1.17	0.55	0.97	1.06	0.21	0.50	0.35
PSD #2	0.62	----	0.58	0.55	0.99	0.48	0.22	1.14
PSD avg	0.64	1.17	0.57	0.76	1.03	0.35	0.36	0.75
Canister	0.71	0.91	0.92	0.60	1.27	1.78	0.59	0.59
p-Cl₂- Benzene:								
PSD #1	1.70	1.62	0.49	2.33	1.07	1.70	0.95	2.69
PSD #2	4.15	----	0.78	2.02	1.41	1.47	1.31	2.62
PSD avg	2.92	1.62	0.64	2.18	1.24	1.59	1.13	2.66
Canister	ND	ND	ND	ND	ND	0.98	0.56	1.09
o-Cl₂- Benzene:								
PSD #1	0.83	0.27	0.25	0.26	0.46	0.20	0.13	0.72
PSD #2	1.24	----	0.41	0.87	0.24	0.17	0.28	0.76
PSD avg	1.04	0.27	0.33	0.57	0.35	0.19	0.21	0.74
Canister	0.33	ND	ND	0.33	1.58	0.37	0.29	0.40

^a --- sample lost during desorption/analysis

ND = Not Detected

Plumbing Schematic for Canister – PSD Analysis

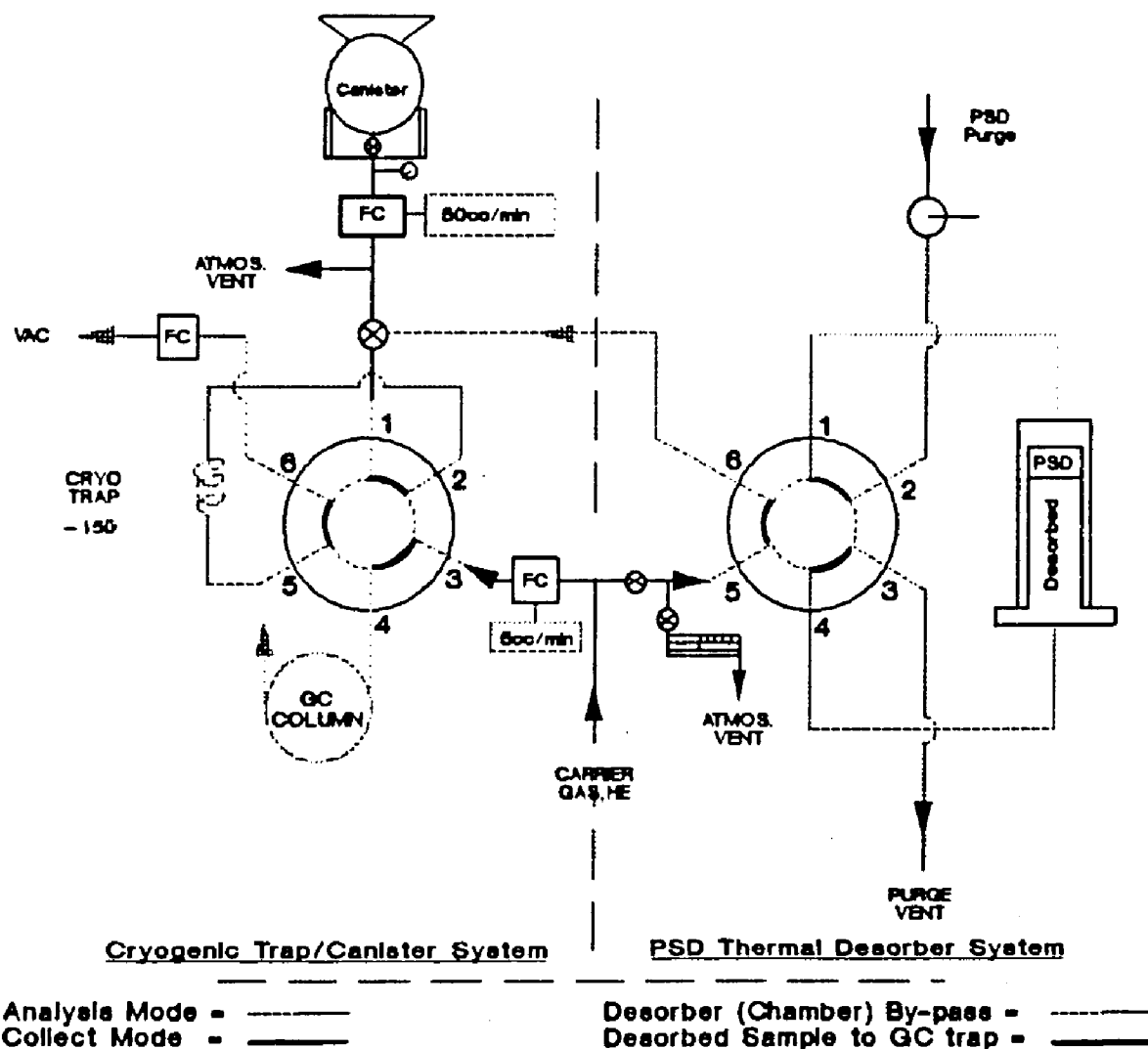


Figure 1. Plumbing pathways for VOC analysis. Collect/analysis valve stages for canister samples (Left side) and desorb/analysis stages for PSD samples (Right side).

CANISTER/PSD SAMPLINGS AT SITE D
1989 DELAWARE FIELD STUDY

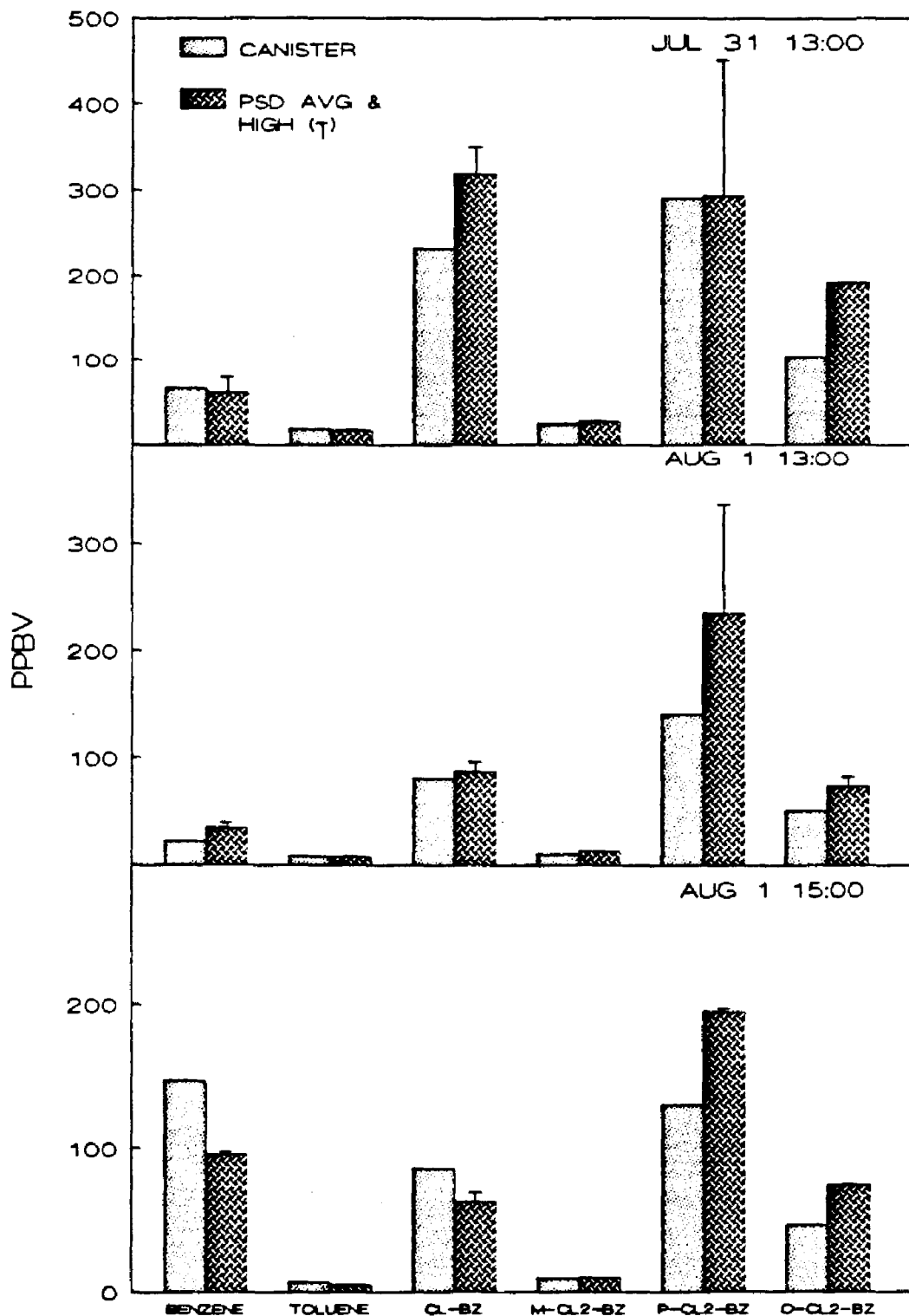


Figure 2. Comparative data of canister and paired PSD samples from three sampling events near an active industrial complex during field study (Site D).

SECTOR SAMPLING FOR VOLATILE ORGANICS CONTRIBUTIONS TO AMBIENT AIR FROM INDUSTRIAL SOURCES

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Sector sampling for volatile organic compounds (VOCs) entails the use of an integrated sampling scheme coupled to a wind direction sensor. Whole air is collected at a constant rate into one of two SUMMA canisters depending upon wind direction; when the wind comes from the suspected emissions area, sample is routed into the "IN" sector canister; otherwise, sample is collected in the "OUT" sector canister. For this set of experiments, the IN and OUT sectors were 90 and 270°, respectively, with the IN sector centered on the VOC source. Two sampling sites were used, the first about two miles north by northeast of a group of industrial facilities, and the second was located about one mile south by southeast of these sources. Sites were alternately operated with duplicate sampling systems. The resultant data comparisons between IN and OUT concurrent samples show good correlations to expected VOC emissions, as determined by grab samples taken within the target area.

Introduction

The U.S. Environmental Protection Agency (EPA) has developed methodology over the past six years for the trace-level determination of certain nonpolar volatile organic compounds (VOCs) in the ambient air. This is based upon the use of SUMMA® polished canisters for collecting whole air samples for subsequent laboratory analysis. Details for the method are available in Method TO-14 of the EPA compendium of methods.¹ Typical applications of TO-14 involve time-integrated point monitoring, usually for 24-h periods, as in EPA's Toxic Air Monitoring System (TAMS) network² or the Urban Air Toxics Monitoring Program (UATMP).³ Though point monitoring has proven to be useful in documenting VOC concentrations, more sophisticated monitoring strategies have been under development to produce additional information such as time variability of VOC concentrations and VOC source locations. This has involved semi-real-time, in situ VOC determination with concurrent wind speed and direction measurement to allow calculation of back trajectories of VOCs,⁴ time-dependent measurements in indoor air situations,⁵⁻⁷ and wind-direction-dependent VOC measurement.⁸

This work concerns the use of a spatially resolved air monitoring strategy for inferring VOC emissions from suspect sources. The philosophy of the method is collection of ambient air into one of two containers, depending upon whether or not the wind is blowing from a sector containing the suspected VOC source. The differences between the "IN" sector sample and the "OUT" sector sample at a single monitoring site will provide candidate VOCs emanating from the IN sector source. In effect, this "Sector" method provides its own background via the OUT sector sample. To corroborate this identification, additional sites can be operated simultaneously at other directions from the suspect source.

This methodology was tested in an airshed containing a cluster of industrial VOC sources. Two fixed monitoring sites were used, one about two miles north by northeast of the sources, the second less than one mile south by southeast, as diagrammed in Figure 1. Each site was operated in duplicate for part of the time. In addition, various grab samples were taken among the sources. The resulting samples were analyzed for a variety of nonpolar volatile organic "toxics" (listed in reference 1) and for C₄ to C₁₀ alkanes. A data interpretation method is presented for the Sector method to deduce the trace-level contributions of the suspected source area to the receptor sites. The grab sample results are presented to confirm these deductions.

Experimental Section

All samples were collected in 6-liter volume stainless steel canisters with internally passivated surfaces. They are often referred to as "SUMMA cans" because of the proprietary internal (SUMMA) passivation procedure used by the manufacturers. Canisters are cleaned prior to sample collection by evacuation to less than 50 μ m Hg at an elevated temperature of 100°C. Quality assurance of the clean-up procedure is performed on a subset of these canisters by filling them with humidified zero air and analyzing for residual contamination. In the field, samples are always collected by starting at the clean-up vacuum (<50 μ m Hg). Details of the use of various configurations of these sampling devices and the associated compound storage stability are available in Method TO-14¹; some additional representative publications are given in the reference section.⁹⁻¹¹ The canisters used for this project were from two manufacturers: SIS, Inc. (Moscow, Idaho) and Biospherics, Inc. (Hillsborough, Oregon).

The sector samplers consist of a conventional "R"-type actively pumped flow configuration^{9,10} with the exception that a three-way valve allows routing

the air sample flow between two canisters. The destination of the flow is dependent upon the wind direction; that is, its routing to one of the two sampling canisters depends upon a signal from a wind sensor that determines whether the air is coming from the suspect source (IN sector) or not (OUT sector). A diagram of this configuration is presented in Figure 2. Three sector samplers from Xontech, Inc. (Van Nuys, CA), were used in this study. Sample flow was maintained at about 10.5 cm³/min, which would result in a final canister pressure of 20 psig after 24 h if the wind direction never changed. Typically, the IN sector canister fills at a lower rate because the respective sector is smaller than that for the OUT canister (90 vs. 270°); sometimes two OUT sector samples are collected before sufficient volume of IN sample is collected for analysis.

For the first two tests, site 1 was operated in duplicate with samplers #1 and 3, and for the remaining two tests, site 2 was operated in duplicate with samplers #2 and 3. The details of the sampling program, times, sites, sampler number, and canister number, are given in Table I.

Two secure sites were provided by the State of Delaware for our experiments; both had electrical power available for the samplers. The sites were in the New Castle area near a variety of industrial sources including a coal-fired power plant, an oil refinery, a petroleum product storage and transfer facility, various chemical manufacturers, and plastics manufacturing plants. The samplers were operated with 90° IN sectors (with corresponding 270° OUT sectors). A diagram of the relative locations of the sources, sampling sites, and the IN sectors is given in Figure 1.

All analyses were performed by gas chromatography/mass spectrometry (GC/MS; Hewlett-Packard [HP] model 5880A gas chromatograph and model HP-5970B mass selective detector, Hewlett-Packard, Avondale, PA, and Palo Alto, CA, respectively) in selected ion monitoring mode for the TO-14 list of 40 nonpolar VOCs. In addition, a flame ionization detector (FID) was used in parallel at the column outlet to determine nontarget compounds, primarily the C₄ to C₁₀ alkanes. Sample was preconcentrated with a Nutech 320-1 cryogenic focussing unit (Nutech, Inc., Durham, NC) and separated on an HP 50-m by 0.32-mm-i.d., HP-1 fused-silica capillary column. Some of the grab samples taken among the sources were analyzed by GC/MS scan methods (28.5 to 350 amu) to identify all major organic constituents. The higher level compounds were then quantified by using a second GC (also an HP-5880A), equipped with an FID and an electron capture detector. The general analytical methods for these analyses are presented in the literature¹²⁻¹⁴; the specific analytical protocols used for the sector sample analyses are identical to those for EPA's TAMS network and are described in detail in the current TAMS report.² Most of the grab samples were taken near a chlorinated compound manufacturer (see Figure 1, source #1); some additional samples were taken very near (and downwind from) the petroleum distiller's tank farm (Figure 1, source 4).

Results and Discussion

Grab samples showed two specific groups of compounds, depending upon location; typical ranges of concentrations are given in Table II for samples taken near the tank farm and near the chlorinated chemicals manufacturer. These compounds were extremely variable in time, and we typically collected only grab samples when there were indications that an "event" was occurring, such as smells, data from real-time instrumentation, or obvious plumes. Most of these samples were taken near the chlorinated chemicals plant, and the results are from mass spectrometry data. The alkane and hydrocarbon data are from a few grab samples taken on a roadway near the oil storage facility and are based upon

approximations from FID traces. Only compounds that exceeded 10 ppbv in at least one sample are listed in the table.

The data from the sector samplers is broken down into two categories, mass spectrometry data for "target compounds," the toxic VOCs as listed in Method TO-14, and data for the alkanes and other hydrocarbons that were taken from FID traces and quantified with respect to a calibrated benzene response.

Cursory inspection of the concentration data reveals that differences between the IN and OUT paired sector samples are subtle and that the concentrations at the sites 1 to 3 miles away from the sources are essentially at background levels. To allow the extraction of useful information from this data set, a parameter for comparing paired IN and OUT sector data on a per compound basis was defined as

$$R = (IN - OUT)/(IN + OUT + 10^{-6}) \quad (1)$$

where IN and OUT are concentrations in parts per billion by volume for specific sample sets and individual compounds. The addition of 10^{-6} in the denominator is a calculational aid to avoid dividing by zero.

The parameter R ranges from -1 to +1 and can accommodate 0 concentration values. Positive R values indicate an IN sector prevalence, whereas negative values indicate an OUT sector prevalence. The absolute value of R gives a relative measure of the importance of a compound in a sector. For example, consider the following cases:

If	Then
IN >> OUT	$R = +1$
IN = 2 OUT	$R = +0.33$
IN = OUT	$R = 0$
IN = 1/2 OUT	$R = -0.33$
IN << OUT	$R = -1$

Because this is a "ratio" parameter, some consideration must be given to dealing with very low concentration values. That is, when the minimum quantifiable level is approached, at which point is a concentration considered zero or some minimum value? These decisions can easily change the calculated R from 0 to ± 1 . This was handled by rounding all data to the nearest 0.1 ppbv (defined as our minimum quantifiable level for this project), generating all the R values, and then generating overall averages of concentrations for each compound from the sector samples. For compounds that exhibited average concentrations at or below the minimum quantifiable level, the R values were not considered as strong indicators of sector prevalence.

Even in the absence of any sources, there will be scatter in the R values from the intrinsic sampling and analytical precision errors. We assumed that such error is normally distributed and derive a measure of significance by calculating a relative standard deviation (RSD) and a mean for various categories of R values. The resulting data can then be interpreted in light of the RSD values; that is, different levels of confidence can be assigned to determinations of whether a compound is emanating from the source sector. In addition, the use of duplicate sampling allows direct comparisons between nominally identical samples. R values and their RSDs calculated for such paired samples can also serve to indicate any system problems with the samplers.

Reduced data from the sector sampling experiments are presented as a compilation of average R values and RSDs on a per compound basis for site 1

(Table III), site 2 (Table IV), and for all data combined (Table V). Data from duplicate samplers are included because these were totally independent concurrent measurements. A third column is added for convenience, in which the ratios of the average R value and the RSD are given. This parameter (statistical significance) is defined as

$$S = R(\text{ave})/RSD \quad (2)$$

and serves as an indicator of the statistical significance of the R value in the following manner:

If	Then
$-0.5 < S < +0.5$	the mean value of R is less than 1/2 standard deviation from the null hypothesis: No statistical difference between IN and OUT sectors
$-1.0 < S < -0.5$ or $+0.5 < S < +1.0$	there exists a moderate statistical difference between IN and OUT sectors: Negative S corresponds to OUT sector, positive S corresponds to IN sector
$S < -1.0$ or $S > 1.0$	there exists a significant statistical difference between IN and OUT sectors: Negative S corresponds to OUT sector, positive S corresponds to IN sector

A similar compilation of information for all the duplicate samples is presented in Table VI; in this case, the S values are measures of overall compound-dependent sampling and analytical scatter. Table VII contains the overall averages of concentrations for each compound.

The information from Tables III through VII is reduced into Table VIII, where statistically significant sector assignments are made. Compounds are labeled as associated with the IN or OUT sector for site 1 or site 2; and for the composite data set, they are labeled both for "moderate" statistical difference and for "significant" statistical difference.

The following "filtering" was applied to the data to arrive at the results in Table VIII:

- Dichloromethane data were deleted because duplicate precision data from Table VI exhibit both a high R value and a large S value; this indicates a systematic problem, possibly contamination.
- Benzene, toluene, and 1,2,4-trimethylbenzene data exhibit S values greater than 0.5 for their duplicate comparisons (Table VI). Because the corresponding R values were all below 0.1 (very close to neutral bias), this indicates scatter in side-by-side sampling without appreciable systematic error. Also, examination of the raw data shows that these compounds were internally consistent within their respective samplers. Therefore, this data was considered useful. The methylpentane isomers were also treated this way.
- Ethyl chloride and vinylidene chloride were deleted from summary Table VIII because the overall average concentration throughout the study was well below the minimum quantifiable level (see Table VII), and they were found during only one sampling episode at low levels.

- Though a few other compounds such as trichlorobenzene, *n*-octane, and *n*-nonane exhibit low average concentrations in Table VII, these data were judged useful and included in Table VIII because they were found in about half the samples at levels exceeding the minimum quantifiable level.

The final results in the summary Table VIII show the following:

- The most "moderate" and "significant" correlations are for site 2; this is expected because this site is closer to the sources, as seen in Figure 1.
- Most of the positive correlation is for the aliphatic and aromatic hydrocarbons; the source area is dominated by petroleum product processing and storage.
- Freon 12 exhibits a definite OUT sector prevalence for site 1 and a moderate IN sector prevalence for site 2. This points out the benefit of using at least two sites when sector-sampling air from a suspected source. In this case, the source of the Freon 12 is apparently somewhere in the IN sector for site 2 but also north or northeast of site 1; therefore, it is not coming from the source area.

Given the data from Table VIII, one can conclude reasonably that the following compounds are candidates of VOC source emissions from the suspect source area:

benzene	trichlorobenzene	3-methylpentane
toluene	isobutane	<i>n</i> -hexane
chlorobenzene	butane	methylcyclopentane
ethylbenzene	isopentane	cyclohexane
<i>m,p</i> -xylene	pentane	isooctane
<i>p</i> -dichlorobenzene	cyclopentane	<i>n</i> -octane
<i>o</i> -dichlorobenzene	2-methylpentane	

When this list is compared to the listing of dominant VOCs found in the grab samples (Table II), we see that every compound from Table II is identified as an emission candidate by the sector sampler method. The additional compounds are likely lower level steady-state source emissions that did not exhibit greater than 10 ppbv levels, or event releases that were missed by the few grab samples.

Conclusions and Recommendations

The sector sampling methodology and the described data reduction techniques can provide VOC data that indicates probable source emission identifications, even at distances of one to three miles. This is a useful technique for both short-term VOC screening of suspect sources and for long-term monitoring of the contributions from a specific source. The method is optimized by the use of multiple sites and by minimizing the distance between the receptor site and the suspect source; distances of one mile or less are recommended.

Acknowledgments

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Table I. Sector Samples – Times and Locations

Time period	Site	Sampler	Canister ^a	
			IN	OUT
11:00 8/1	1	1	11	05, 50
17:10 8/3	1	3	02	74, 08
	2	2	77	24, 42
17:15 8/3	1	1	23	14
9:20 8/5	1	3	46	32
	2	2	73	64
10:30 8/5	1	1	75	53
17:18 8/6	2	2	62	35
	2	3	11	16
17:25 8/6	1	1	75	76, 31
14:00 8/8	2	2	71	48, 13
	2	3	65	45, 44

^aBecause of wind conditions, canister #75 serves as IN sample for P4 site for last two time periods.

Table II. Results from Grab Samples: Compounds Found at Levels Higher than Typical Background Concentrations

Chlorinated chemicals manufacturer (mass spectrometer data)		Petroleum products storage/handling facility (approx. FID data)	
Compound	ppbv Range (10 samples)	Compound	ppbv Range (2 samples)
dichloromethane	1 – 12	butane	22 – 103
benzene	1 – 51	isopentane	13 – 444
chlorobenzene	7 – 260	pentane	7 – 200
<i>p</i> -dichlorobenzene	12 – 247	2-methylpentane	2 – 50
<i>o</i> -dichlorobenzene	4 – 154	3-methylpentane	2 – 25
trichlorobenzene	1 – 41	methylcyclopentane	1 – 13

Table III. IN vs OUT Comparisons – Site 1^a

<i>R</i> (ave)	RSD	Compound	<i>S</i>
-0.230	0.217	FREON 12	-1.060
-0.169	0.269	METHYLCHLORID	-0.628
-0.333	0.516	ETHYLCHLORIDE	-0.645
-0.056	0.078	FREON 11	-0.715
0.000	0.000	VINYLDIENECHL	ERR
-0.008	0.101	DICHLOMETHANE	-0.080
0.129	0.231	FREON 113	0.557
0.063	0.211	METHYLCHLFORM	0.296
0.067	0.075	BENZENE	0.898
-0.081	0.151	CARBONTETCHLO	-0.536
-0.005	0.090	TOLUENE	-0.051
0.433	0.496	CHLOROBENZENE	0.873
0.094	0.162	ETHYLBENZENE	0.583
0.073	0.199	<i>m,p</i> -XYLENE	0.367
-0.006	0.266	<i>o</i> -XYLENE	-0.022
-0.333	0.816	4-ETHYLTOLUEN	-0.408
0.000	0.632	1,3,5-METBENZ	0.000
0.043	0.246	1,2,4-METBENZ	0.176
0.230	0.694	<i>p</i> -DICHLORBENZ	0.332
0.056	0.136	<i>o</i> -DICHLORBENZ	0.408
0.000	0.000	TRICHLBENZENE	ERR
0.094	0.170	ISOBUTANE	0.556
0.149	0.129	BUTANE	1.152
0.171	0.107	ISOPENTANE	1.596
0.135	0.080	PENTANE	1.673
0.239	0.428	CYCLOPENTANE	0.559
0.165	0.115	2-METHPENTANE	1.437
0.229	0.140	3-METHPENTANE	1.640
0.096	0.161	<i>n</i> -HEXANE	0.594
0.178	0.150	METHCYCPENTAN	1.185
0.113	0.138	CYCLOHEXANE	0.816
0.029	0.129	ISOOCTANE	0.228
-0.087	0.466	<i>n</i> -HEPTANE	-0.187
0.056	0.646	<i>n</i> -OCTANE	0.086
0.134	0.992	<i>n</i> -NONANE	0.135
0.072	0.366	<i>n</i> -DECANE	0.197

^aAbbreviations are $R = (IN - OUT)/(IN + OUT + 10^{-6})$, RSD = relative standard deviation, $S = R(ave)/RSD$

Table IV. IN vs OUT Comparisons – Site 2^a

<i>R</i> (ave)	RSD	Compound	<i>S</i>
0.239	0.378	FREON 12	0.632
0.016	0.139	METHYLCHLORID	0.114
0.000	0.000	ETHYLCHLORIDE	ERR
-0.009	0.075	FREON 11	-0.115
-0.166	0.407	VINYLDENECHL	-0.408
0.039	0.045	DICHLOMETHANE	0.868
-0.175	0.406	FREON 113	-0.431
-0.032	0.086	METHYLCHLFORM	-0.374
0.170	0.088	BENZENE	1.925
0.048	0.223	CARBONTETCHLO	0.213
0.144	0.049	TOLUENE	2.952
0.395	0.128	CHLOROBENZENE	3.083
0.122	0.142	ETHYLBENZENE	0.858
0.161	0.048	<i>m,p</i> -XYLENE	3.328
0.142	0.128	<i>o</i> -XYLENE	1.113
0.079	0.137	4-ETHYLTOLUEN	0.580
-0.198	0.633	1,3,5-METBENZ	-0.313
0.102	0.128	1,2,4-METBENZ	0.797
0.350	0.203	<i>p</i> -DICHLORBENZ	1.721
0.342	0.198	<i>o</i> -DICHLORBENZ	1.727
0.683	0.402	TRICHLBENZENE	1.700
0.449	0.188	ISOBUTANE	2.383
0.352	0.166	BUTANE	2.120
0.306	0.097	ISOPENTANE	3.164
0.304	0.152	PENTANE	2.001
0.555	0.501	CYCLOPENTANE	1.107
0.291	0.164	2-METHPENTANE	1.777
0.250	0.122	3-METHPENTANE	2.044
0.342	0.159	<i>n</i> -HEXANE	2.148
0.190	0.165	METHCYCPENTAN	1.155
0.250	0.204	CYCLOHEXANE	1.225
0.261	0.169	ISOOCTANE	1.543
0.278	0.389	<i>n</i> -HEPTANE	0.713
0.611	0.443	<i>n</i> -OCTANE	1.380
0.111	0.172	<i>n</i> -NONANE	0.645
0.190	0.268	<i>n</i> -DECANE	0.712

^aAbbreviations are $R = (IN - OUT)/(IN + OUT + 10^{-6})$, RSD = relative standard deviation,
 $S = R(ave)/RSD$

Table V. IN vs OUT Comparisons – Combined Data Set^a

R (ave)	RSD	Compound	S
0.004	0.383	FREON 12	0.011
-0.076	0.226	METHYLCHLORID	-0.338
-0.167	0.389	ETHYLCHLORIDE	-0.428
-0.032	0.077	FREON 11	-0.419
-0.083	0.288	VINYLDENECHL	-0.289
0.015	0.079	DICHLOMETHANE	0.197
-0.023	0.353	FREON 113	-0.065
0.015	0.162	METHYLCHLFORM	0.094
0.119	0.095	BENZENE	1.254
-0.017	0.194	CARBONTETCHLO	-0.086
0.070	0.104	TOLUENE	0.672
0.414	0.346	CHLOROBENZENE	1.196
0.108	0.146	ETHYLBENZENE	0.741
0.117	0.146	<i>m,p</i> -XYLENE	0.804
0.068	0.214	<i>o</i> -XYLENE	0.318
-0.127	0.598	4-ETHYLTOLUEN	-0.212
-0.099	0.612	1,3,5-METBENZ	-0.162
0.073	0.190	1,2,4-METBENZ	0.384
0.290	0.492	<i>p</i> -DICHLORBENZ	0.590
0.199	0.221	<i>o</i> -DICHLORBENZ	0.901
0.341	0.448	TRICHLBENZENE	0.762
0.272	0.252	ISOBUTANE	1.078
0.250	0.177	BUTANE	1.414
0.239	0.120	ISOPENTANE	1.984
0.219	0.146	PENTANE	1.504
0.397	0.474	CYCLOPENTANE	0.838
0.228	0.150	2-METHPENTANE	1.520
0.239	0.125	3-METHPENTANE	1.906
0.219	0.199	<i>n</i> -HEXANE	1.096
0.184	0.150	METHCYCPENTAN	1.224
0.181	0.181	CYCLOHEXANE	1.002
0.145	0.188	ISOOCTANE	0.774
0.095	0.451	<i>n</i> -HEPTANE	0.211
0.333	0.602	<i>n</i> -OCTANE	0.553
0.122	0.679	<i>n</i> -NONANE	0.180
0.131	0.312	<i>n</i> -DECANE	0.421

^aAbbreviations are $R = (IN - OUT)/(IN + OUT + 10^{-6})$, RSD = relative standard deviation, $S = R(ave)/RSD$

Table VI. Duplicate Samples Comparisons^a

R (ave)	RSD	Compound	S
0.113	0.319	FREON 12	0.354
0.001	0.206	METHYLCHLORID	0.007
0.000	0.000	ETHYLCHLORIDE	ERR
0.034	0.074	FREON 11	0.466
0.000	0.000	VINYLDIENECHL	ERR
-0.350	0.287	DICHLOMETHANE	-1.218
0.016	0.433	FREON 113	0.038
0.006	0.110	METHYLCHLFORM	0.058
0.063	0.064	BENZENE	0.972
0.067	0.211	CARBONTETCHLO	0.316
0.029	0.047	TOLUENE	0.624
0.052	0.191	CHLOROBENZENE	0.274
0.000	0.094	ETHYLBENZENE	0.000
0.006	0.054	<i>m,p</i> -XYLENE	0.103
-0.002	0.151	<i>o</i> -XYLENE	-0.015
0.020	0.475	4-ETHYLTOLUEN	0.042
0.033	0.483	1,3,5-METBENZ	0.069
0.084	0.161	1,2,4-METBENZ	0.524
-0.156	0.589	<i>p</i> -DICHLORBENZ	-0.265
-0.180	0.436	<i>o</i> -DICHLORBENZ	-0.412
0.014	0.045	TRICHLBENZENE	0.316
0.021	0.074	ISOBUTANE	0.288
0.011	0.069	BUTANE	0.162
0.015	0.063	ISOPENTANE	0.233
0.026	0.064	PENTANE	0.411
-0.036	0.482	CYCLOPENTANE	-0.075
-0.044	0.061	2-METHPENTANE	-0.723
-0.038	0.068	3-METHPENTANE	-0.559
0.015	0.086	<i>n</i> -HEXANE	0.172
-0.048	0.110	METHCYCPENTAN	-0.433
0.000	0.094	CYCLOHEXANE	0.000
0.137	0.313	ISOOCTANE	0.437
0.133	0.322	<i>n</i> -HEPTANE	0.414
0.100	0.316	<i>n</i> -OCTANE	0.316
0.000	0.471	<i>n</i> -NONANE	0.000
-0.001	0.195	<i>n</i> -DECANE	-0.006

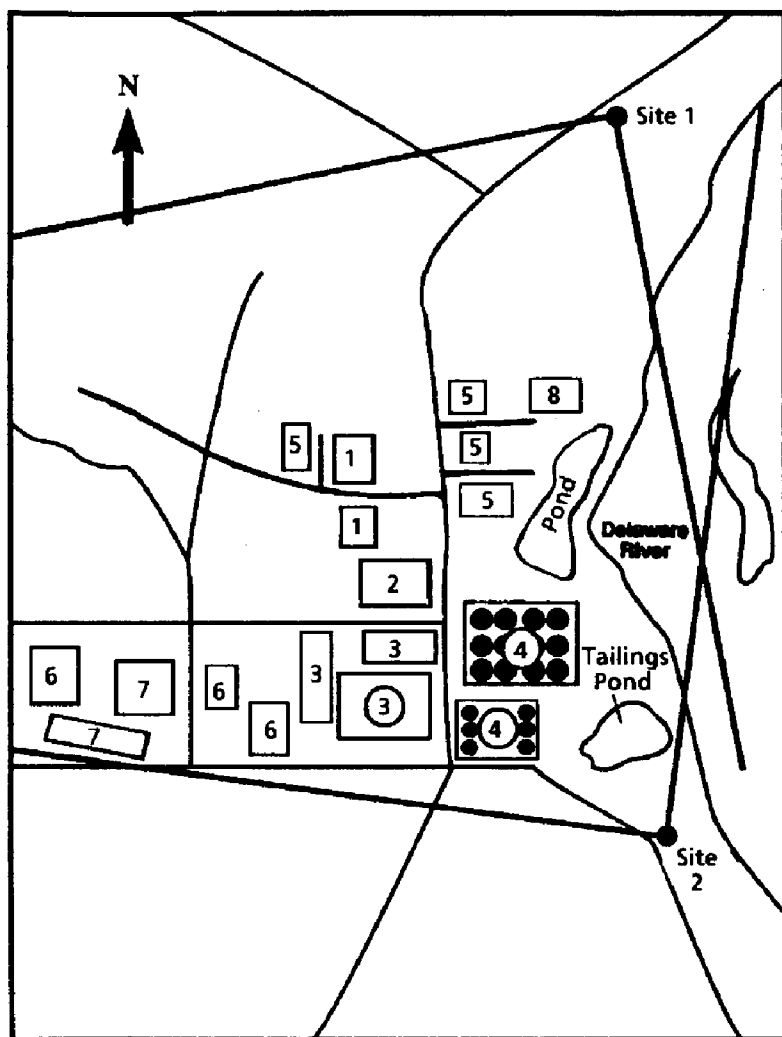
^aAbbreviations are $R = (IN - OUT)/(IN + OUT + 10^{-6})$, RSD = relative standard deviation, $S = R(ave)/RSD$

Table VII. Average Concentrations Measured – Total Data Set

Compound	ave ppbv	Compound	ave ppbv
FREON 12	0.52	ISOBUTANE	1.20
METHYLCHLORID	0.49	BUTANE	2.22
ETHYLCHLORIDE	0.02	ISOPENTANE	2.37
FREON 11	0.33	PENTANE	1.05
VINYLDENECHL	0.00	CYCLOPENTANE	0.09
DICHLOMETHANE	0.99	2-METHPENTANE	0.53
FREON 113	19.98	3-METHPENTANE	0.37
METHYLCHLFORM	0.48	<i>n</i> -HEXANE	0.32
BENZENE	0.58	METHCYCPENTAN	0.17
CARBONTETCHLO	0.14	CYCLOHEXANE	0.15
TOLUENE	0.99	ISOOCTANE	0.19
CHLOROBENZENE	0.25	<i>n</i> -HEPTANE	0.11
ETHYLBENZENE	0.18	<i>n</i> -OCTANE	0.07
<i>m,p</i> -XYLENE	0.56	<i>n</i> -NONANE	0.05
<i>o</i> -XYLENE	0.23	<i>n</i> -DECANE	0.22
4-ETHYLTOLUEN	0.09		
1,3,5-METBENZ	0.09		
1,2,4-METBENZ	0.27		
<i>p</i> -DICHLORBENZ	0.61		
<i>o</i> -DICHLORBENZ	0.13		
TRICHLBENZENE	0.04		

Table VIII. Reduced Sector Data – Compounds Assigned to IN or OUT Sectors

Compound	Moderate stat. sign.			Significant stat. sign.		
	Site 1	Site 2	Combined data set	Site 1	Site 2	Combined data set
FREON 12	OUT	IN	–	OUT	–	–
METHYLCHLORID	OUT	–	–	–	–	–
FREON 11	OUT	–	–	–	–	–
FREON 113	IN	–	–	–	–	–
METHYLCHLFORM	–	–	–	–	–	–
BENZENE	IN	IN	IN	–	IN	IN
CARBONTETCHLO	OUT	–	–	–	–	–
TOLUENE	–	IN	IN	–	IN	–
CHLOROBENZENE	IN	IN	IN	–	IN	IN
ETHYLBENZENE	IN	IN	IN	–	–	–
<i>m,p</i> -XYLENE	–	IN	IN	–	IN	–
<i>o</i> -XYLENE	–	IN	–	–	IN	–
4-ETHYLTOLUEN	–	IN	–	–	–	–
1,3,5-METBENZ	–	–	–	–	–	–
1,2,4-METBENZ	–	IN	–	–	–	–
<i>p</i> -DICHLORBENZ	–	IN	IN	–	IN	–
<i>o</i> -DICHLORBENZ	–	IN	IN	–	IN	–
TRICHLBENZENE	–	IN	IN	–	IN	–
ISOBUTANE	IN	IN	IN	–	IN	IN
BUTANE	IN	IN	IN	IN	IN	IN
ISOPENTANE	IN	IN	IN	IN	IN	IN
PENTANE	IN	IN	IN	IN	IN	IN
CYCLOPENTANE	IN	IN	IN	–	IN	–
2-METHPENTANE	IN	IN	IN	IN	IN	IN
3-METHPENTANE	IN	IN	IN	IN	IN	IN
<i>n</i> -HEXANE	IN	IN	IN	–	IN	IN
METHCYCPENTAN	IN	IN	IN	IN	IN	IN
CYCLOHEXANE	IN	IN	IN	–	IN	IN
ISOOCTANE	–	IN	IN	–	IN	–
<i>n</i> -HEPTANE	–	IN	–	–	–	–
<i>n</i> -OCTANE	–	IN	IN	–	IN	–
<i>n</i> -NONANE	–	IN	–	–	–	–
<i>n</i> -DECANE	–	IN	–	–	IN	–



1. Chlorinated Chemical Manufacturer
2. Power Plant (Coal)
3. Oil Refinery
4. Oil Tank Farm
5. Chemical Company
6. Liquified Gas Manufacturer
7. Plastics Manufacturer
8. Truck Depot

Figure 1. Diagram of relative locations of sector sampling sites and the suspect sources.

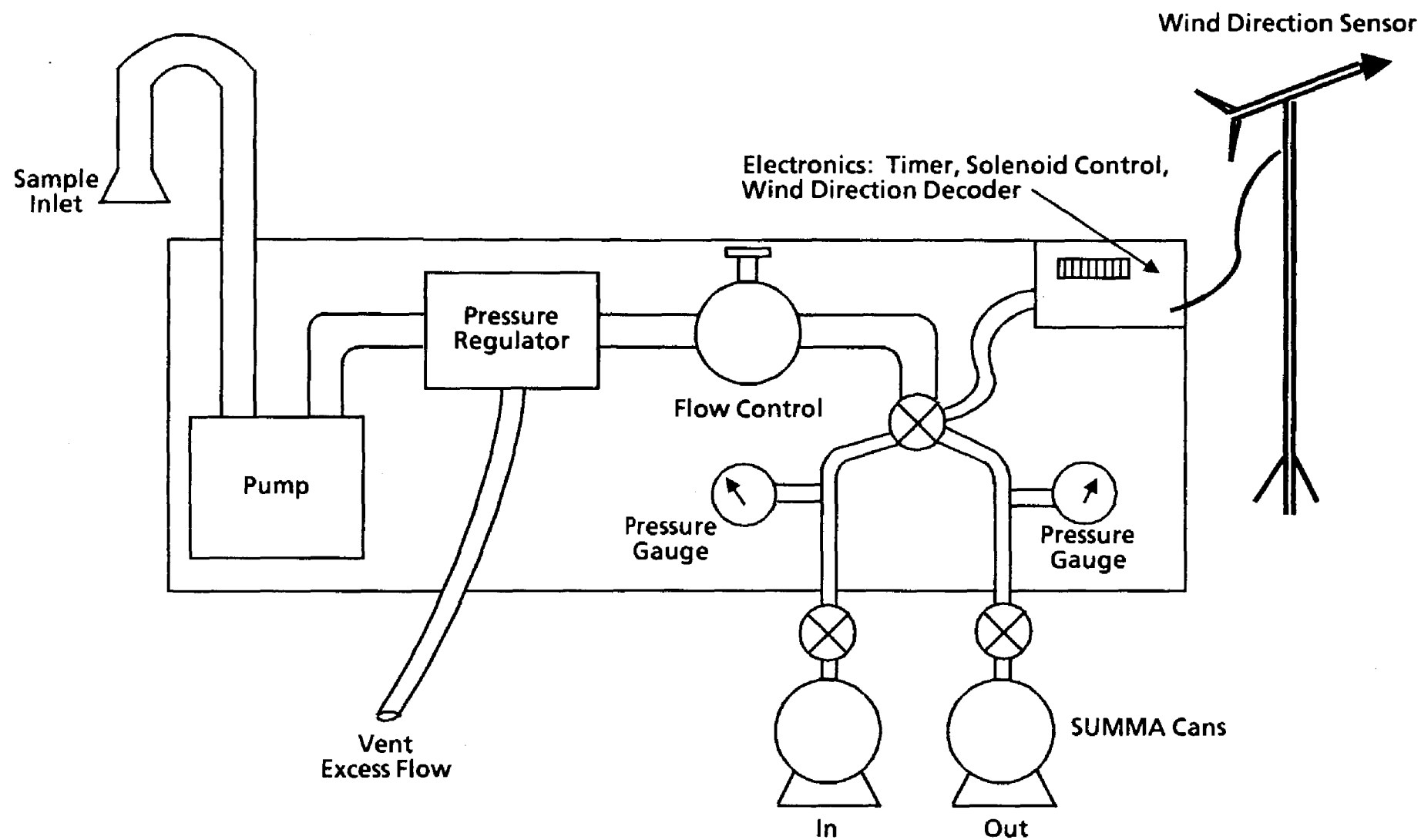


Figure 2. Schematic of sector sampler flow arrangement.

Remote FTIR Measurement of Chemical Emissions

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We have made longpath FTIR measurements as part of a study sponsored by the Superfund Innovative Technology Evaluation (SITE) program. The purpose of the study was to compare concentrations measured by the FTIR remote sensor with those measured, by GC/MS techniques, on samples collected in canisters. The concept of the FTIR system is based on the Remote Optical Sensing of Emissions (ROSE) system, designed by W. F. Herget.¹ The current system is a design variation which uses a single telescope to both transmit the ir probe beam and to receive the return beam reflected from a retroreflector placed out in the field. A Cassagrain telescope with a 37 cm primary mirror is directed at a remotely located retroreflector. This arrangement simplifies system alignment as compared to the original ROSE system. A Nicolet Model 730 FTIR system is coupled to the telescope with appropriate transfer optics. Other advantages of the current system are smaller overall size, much greater disk storage capacity, and a computerized concentration calculation program which performs a classical least squares fit of absorption bands to precisely measured reference spectra.

For the subject program, the FTIR remote sensor was mounted in the rear of an airconditioned motor vehicle. The telescope was aimed out through an open window. The measurements were made at seven sites in the vicinity of New Castle, Delaware. Total path lengths ranged from 250 to 1022 meters. Elevated levels of methane were measured along with ammonia, in the vicinity of a municipal incinerator landfill site. Chlorobenzene and p-dichlorobenzene were measured in the vicinity of a chemical plant. Simultaneous canister collections of the chlorobenzenes were made to test the accuracy of the remote sensor; these are presented in another paper by Russwurm and McClenny.²

File Name	Time	Pathlength (meters)	No. of Sweeps	Methane (ppm)	CO (ppb)	p-dichlbenzene (ppb)	Chlorobenzene (ppb)
A00731.001	10:51:03	374	256	1.38(22)	90(160)	62(11)	
A00731.002	11:48:28	374	64	1.60(13)	400(240)	37.5(6.0)	46(32)
A00731.003	11:52:53	374	64	1.56(12)	290(170)	31.6(6.3)	80(31)
A00731.004	11:57:36	374	64	1.58(12)	310(180)	31.2(6.3)	36(31)
A00731.005	12:02:27	374	64	1.63(12)	410(230)	51.9(4.9)	39(24)
A00731.007	12:28:20	374	64		190(100)	62.1(6.3)	88(33)
A00731.008	12:32:47	374	64	1.58(12)	250(140)	41.0(7.4)	43(35)
A00731.009	12:36:52	374	64	1.58(12)	200(100)	44.2(6.3)	85(33)
A00731.010	12:41:05	374	64	1.57(12)	390(210)	47.4(5.6)	64(32)
A00731.012	13:54:59	374	16	1.56(12)	190(110)	40.3(9.8)	52(47)
A00731.013	13:57:16	374	16	1.54(12)	190(100)	61.7(9.1)	63(47)
A00731.014	14:00:48	374	16	1.54(11)	280(160)	70.1(8.4)	157(46)
A00731.015	14:03:32	374	16	1.53(12)	500(280)	45.2(8.4)	129(38)
A00731.016	14:43:59	374	256	1.48(12)	290(170)	58.9(7.0)	41(33)
A00731.017	15:12:22	374	256	1.48(12)	300(170)	76.5(7.7)	70(41)
A00731.018	15:38:06	374	64	1.47(12)	270(160)	108(13)	92(46)
A00731.019	15:41:14	374	64	1.45(12)	310(170)	58.6(9.5)	108(53)
A00731.020	15:44:12	374	64	1.47(12)	260(150)	74.4(9.8)	90(46)
A00731.021	15:47:18	374	64	1.47(12)	260(150)	59(10)	
A00731.022	15:50:17	374	64	1.50(12)	380(200)	73.3(7.4)	64(37)
A00731.023	15:53:18	374	64	1.45(12)	280(160)	49(10)	143(53)
A00731.024	15:56:16	374	64	1.46(12)	290(160)	77.5(9.5)	
A00731.025	15:59:22	374	64	1.46(12)	350(200)	54(10)	70(51)
A00731.026	16:02:25	374	64	1.46(13)	200(120)	70(10)	
A00731.027	16:05:33	374	64	1.48(13)	200(110)	109(10)	50(50)
A00731.028	16:08:50	374	64	1.50(13)	230(120)	121(12)	
A00731.029	16:11:57	374	64	1.50(13)	180(110)	202(13)	
A00731.032	17:51:28	376	64	1.58(14)	220(150)	249(13)	420(71)
A00731.033	17:59:34	376	64	1.56(17)	210(170)	260(16)	840(81)
A00731.034	18:04:36	376	64	1.57(17)	200(160)	206(13)	398(72)
A00731.035	18:08:20	376	64		220(160)	171(16)	405(81)
A00731.036	18:20:37	376	256		270(190)	219(12)	109(60)
A00731.037	18:48:08	376	128	1.49(15)	260(200)	137(10)	110(100)
A00731.038	19:12:36	376	64	1.82(18)	240(180)	221(12)	65(54)
A00731.039	19:16:23	376	64	1.85(19)	240(190)	183(11)	120(100)
A00731.040	19:19:34	376	64	1.85(19)	300(240)	132(10)	
A00731.041	19:22:33	376	64	1.85(19)	310(250)	165(12)	
A00731.042	19:25:34	376	64	1.75(18)	240(190)	177(12)	
A00731.043	19:28:44	376	64	1.54(16)	260(200)	116(10)	130(110)
A00731.044	19:31:43	376	64	1.50(15)	280(110)	109(12)	250(140)
A00731.045	19:34:48	376	64	1.49(16)	240(180)	120(12)	
A00731.046	19:37:47	376	64	1.49(15)	300(230)	123(12)	210(140)
A00731.047	19:40:47	376	64	1.50(16)	220(170)	144(11)	130(110)
A00731.048	19:43:45	376	64	1.48(16)	330(260)	155(11)	

Table 1 Concentration Values for measurements made at in vicinity of the Standard Chlorine Chemical plant on July 31, 1989. The numbers in the parenthese are the estimated standard deviation of the least squares fit propagated to the concentrations determinations.

The FTIR remote measurements were made at seven different locations, in the vicinity of New Castle, Delaware, on ten different days. Figure 1 shows the unistatic configuration used for these measurements. We were able to measure the ambient levels of the normal atmospheric constituents, carbon monoxide and methane, in any configuration in respect to the wind direction. Measurements of the chemicals emitted from local sources, however, requires that at least part of the ir beam intersect the down-wind flow of air from a source. Several days of field measurements in the vicinity of the chemical plant gave no results for local emissions because of unfavorable wind directions. On the second week when the wind direction shifted, we returned to the chemical plant and made measures at a site which was clearly down-wind from chemical waste stacks. Analysis of the spectra produced by the FTIR sensor indicated the presence of chlorobenzene and p-dichlorobenzene, and we made quantitative measurements for two days at this site. The results are shown in Tables 1 and 2. The numbers in the parenthese are the estimated standard deviations of the least squares fit propagated to the the concentration determination. These numbers are relative to the last digit in the concentration. The results for p-dichlorobenzene are the weighted average of determinations made from a least squares fit of the field spectrum to three different absorption bands, and the results for chlorobenzene is the weighted average of determinations made from two different absorption bands.

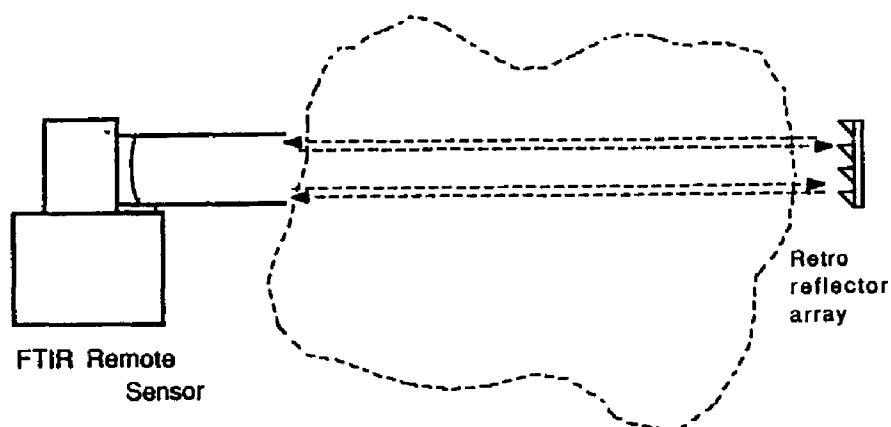


Figure 1. The Unistatic FTIR Remote Measurement Configuration.

On a subsequent measurement day, we set up the remote sensor at two different sites at the Pigeon Point incinerator and landfill facility. Here we had flexibility to configure the measurement downwind of probable emission sources. The results of all the measurement made at Pigeon Point is shown in Table 3. At the first site, which was down-wind to a methane burning flare, we measured elevated quantities of methane up to 8.1 ppm. We moved to the second site, which was in the vicinity of solid waste digestors, and in the first measurement obtained a concentration of 200 ppb of ammonia in addition to an elevated concentration of methane of 3.6 ppm. In the subsequent measurements, we no longer obtained results for ammonia, and the concentration of methane approached ambient levels.

After a cursory investigation, we estimate that the accuracy in the FTIR remoter sensor determined concentration is ~ 15 percent in cases where the concentrations are not too close to the minimum detectable limits. This applies to our determinations for p-dichlorobenzene, ammonia, and methane. We plan a more thorough investigation into the various sources of error, in the future, in order to better determine the remote sensor's accuracy. As is discussed by Russwurm and McClenny,² the results for the comparison of the p-dichlorobenzene concentrations determined by the FTIR remoter sensor to those determined from the analysis of simulataneous canister collections showed agreement better than the estimated uncertainties of either technique.

References

1. W. F. Herget and J. D. Brasher, "Remote measurement of gaseous pollutant concentrations using a mobile Fourier Transform interferometer system," *Applied Optics*, **18**, 3404 (1979).
2. G. M. Russwurm, and W. A. McClenny, "A comparison of FTIR open path ambient data with method TO-14 canister data," 1990 EPA/A&WMA International Symposium on Measurement of Toxic and Related Air Pollutants, Raleigh, NC (April 30 - May 4, 1990).

File Name	Time	Pathlength (meters)	No. of Sweeps	Methane (ppm)	CO (ppb)	p-diChlBenzene (ppb)	Chlorobenzene (ppb)
A00801.001	10:23:55	372	256	1.75(14)	330(190)	295(19)	
A00801.002	10:56:16	372	128	1.70(14)	320(180)	104(21)	
A00801.003	11:12:15	372	128	1.67(14)	300(170)	141(25)	
A00801.004	11:18:29	372	128	1.58(14)	270(150)	56(22)	
A00801.005	11:24:22	372	128	1.58(13)	320(180)	60(40)	
A00801.006	11:30:17	372	128	1.57(13)	290(160)	71(24)	
A00801.007	11:36:18	372	128		300(170)	69(23)	
A00801.009	12:19:42	372	128		270(140)	45(26)	
A00801.010	12:25:32	372	128	1.61(13)	260(140)	45(26)	
A00801.011	12:31:23	372	128	1.60(13)	250(130)	27(26)	
A00801.012	12:37:19	372	128	1.61(14)	260(140)	78(24)	77(42)
A00801.013	12:43:24	372	128	1.61(13)	280(140)	52(26)	45(44)
A00801.014	14:38:47	372	128	1.61(13)	210(110)		
A00801.015	15:55:11	372	128	1.64(12)	200(100)	102(20)	

Table 2 Concentration Values for measurements made at in vicinity of the Standard Chlorine Chemical plant on August 1, 1989. The numbers in the parenthese are the estimated standard deviation of the least squares fit propagated to the concentrations determinations.

File Name	Site	Time	Pathlength (meters)	No. of Sweeps	Methane (ppm)	CO (ppb)	Ammonia (ppm)
A00802.001	Pigeon Point 1	10:04:42	312	256	7.2(4)	220(150)	
A00802.003		11:29:32	312	256	8.12(37)	200(130)	
A00802.005		12:01:15	312	128	7.04(35)	240(140)	
A00802.006		12:07:43	312	128	7.7(4)	210(130)	
A00802.007		12:13:56	312	128	6.42(38)	220(140)	
A00802.008		12:19:52	312	128	5.74(32)	230(140)	
A00802.009		12:25:42	312	128		240(140)	
A00802.011		13:18:43	312	256		130(70)	
A00802.013		14:26:55	312	256	6.7(4)	90(60)	
A00802.014	Pigeon Point 2	15:48:12	309	256	3.57(20)	340(150)	203(19)
A00802.016		16:38:18	309	128	1.80(15)	260(130)	
A00802.017		16:52:04	309	128	2.96(32)	260(190)	
A00802.018		16:57:58	309	128	2.08(14)	350(160)	
A00802.019		17:03:50	309	128	1.87(13)	310(150)	
A00802.020		17:09:41	309	128	2.77(18)	380(180)	
A00802.021		17:15:54	309	128	1.84(13)	330(150)	

Table 3 Concentration Values for measurements made at the Pigeon Point municipal waste treatment plant on August 2, 1989. The numbers in the parenthese are the estimated standard deviation of the least squares fit propagated to the concentrations determinations.

A COMPARISON OF FTIR OPEN PATH AMBIENT DATA WITH METHOD TO-14 CANISTER DATA

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In order to determine the effectiveness of a Fourier transform infrared (FTIR) spectrometer used as an open path monitor, a series of experiments were conducted in the vicinity of New Castle, Delaware. Chlorobenzene and *p*-dichlorobenzene data from the FTIR was compared with data obtained by collecting canister samples and performing gas chromatography/mass spectrometry (GC/MS) analyses. To adequately cover the path used by the FTIR, the canister was transported along the path on a bicycle for approximately one-half hour, and the FTIR data were averaged over this time period. The *p*-dichlorobenzene data shows excellent agreement with the canister data, and the bicycle technique seems to lend itself well to such comparisons.

Introduction

One of the requirements of the Superfund Innovative Technology Evaluation program is to compare new, emerging methods with older more mature techniques. In this case the new technology was an FTIR long-path monitor, and the more mature technique was the SUMMA polished canister technique, method TO-14. The FTIR makes path-integrated measurements over physical paths that can be up to 1 km long, whereas the canister technique is inherently a point monitoring method. This primary difference in the two techniques creates difficulties with determining a strategy for comparison sampling because of the spatial and temporal variations in concentration along the path. This study was part of the Delaware field program and the data were taken in an industrial complex south of New Castle.

Results and Discussion

Figure 1 shows a possible configuration of the infrared beam and the plume emanating from a point source. As the distance between the source and the path becomes smaller, the ratio of the plume dimensions to the path length also becomes smaller. This implies that the path-integrated measurement made by the FTIR will also become smaller, and it can indeed drop lower than the detection limits of the instrument. The plume can also be moved along the path by the winds. These conditions were definitely seen during the Delaware study and had been anticipated beforehand. One condition that had not been anticipated was that the plume can move vertically in and out of the path rapidly. The initial sampling strategy was to take relatively long (16-min) FTIR scans to enhance the signal-to-noise ratio. However, when the plume is moving in and out of the path rapidly, the long averaging process can lower the signal sufficiently to obviate any perceived advantages. Because of this, the sampling time for the FTIR was changed in the field to a 4-min period, during which 256 scans were coadded with the FTIR.

In an attempt to overcome the anticipated variability of the concentration along the path for comparison purposes, it had been decided to mount the canister on a bicycle and ride it along the path. Because the transit time with the bicycle is long compared to 4 min and we wanted to cover the path many times during any one sampling period, we extended the sampling time to 32 min. Thus for comparison purposes eight 4-min runs with the FTIR were coadded, and the bicycle was ridden along the path for 32 min. It was felt necessary to transport the canister along the path at a uniform speed, and after a few trial runs this became quite easy to do. As a check, a stopwatch was mounted on the handlebar of the bicycle so that the rider could keep track of the total elapsed time and the time for any path traversal.

Table I shows the concentrations of various gases taken with three canisters equally spaced along the path. These samples were taken simultaneously as grab samples (about 10 sec) and were at intervals of about 30 m. During this period, some odors were detected at one end of the path but not the other, and the data clearly shows concentration variations up to about a factor of 50. Shortly after these samples were taken, the odor disappeared, being there one instant and gone the next.

During the study, only two compounds were detected at concentrations and durations that were sufficient to provide comparison data between the FTIR and the canisters. These were chlorobenzene and *p*-dichlorobenzene. Other data was collected that could be used as a quality control check for the mobile canister technique. This data allowed three comparisons to be made with the canisters alone. Table II shows the results of these comparisons. Column 1 gives the ratio of the average value

obtained from five canisters placed along the path to the value of the concentration measured with a canister transported along the path. Column 2 gives the ratio of various concentrations obtained from two canisters taken simultaneously with the bicycle. At two of the sites, it was impossible to ride the bicycle because of the terrain, and we transported the canisters along the path on foot. When this was done, two persons simultaneously started from opposite ends of the path and carried the canisters for the 32-min period. The results of this comparison are shown in column 3, and although the concentrations were all quite low, they compared well. Column 2, the bicycle duplicate, probably indicates the comparison that can be expected with the canister method. It thus serves to indicate what should be considered an acceptable level for other comparisons. The comparison shown in column 3 indicates very little temporal variability, at least during these sampling periods.

Figure 2 shows the comparison between the canisters and the FTIR for chlorobenzene. Although this shows a higher degree of variability than we would like, the comparison seems adequate. The variability may very well be caused by the fact that the concentrations were close to the detection limits for the FTIR.

Figure 3 shows the results of five comparisons between the FTIR and the canisters. This comparison is excellent and covers a large range of concentrations. It clearly shows that the FTIR can make very good measurements when the concentrations are greater than the detection limits and when the spectra are free of interferences.

Conclusions

Two conclusions can be drawn from this work. They are that the bicycle method for transporting the canisters along the path to make long-path comparisons seems to work well as long as the plume is fairly well behaved over extended (30-min) periods. The second is that the FTIR remote sensing technique seems to be a viable technique for making long-path, open air measurements for some of the volatile organic compounds.

Disclaimer

Although the research described in this article has been funded wholly or in part by the United States Environmental Protection Agency through Contract 68-02-4444 to NSI Technology Services Corporation, it has not been subjected to Agency review and therefore does not necessarily reflect the views of the Agency, and no official endorsement should be inferred. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Table I. Grab Sample Concentrations Taken Along Path (ppb)

Compound	Can A	Can B	Can C
Dichlorodifluoromethane	5.4	0.02	0.05
Benzene	1.5	10.5	50.9
Chlorobenzene	7.1	63.8	263.2
<i>m</i> -Dichlorobenzene	0.5	2.7	26.6
<i>p</i> -Dichlorobenzene	11.6	152.5	247.5
<i>o</i> -Dichlorobenzene	3.9	32.7	154.1
1,2,4-Trichlorobenzene	0.8	21.5	40.9

Table II. Canister Comparison Ratios¹

Compound	Path Avg. ²	Bicycle Duplicates	Walking Duplicates
Dichlorodifluoromethane	0.47	1.0	1
Methyl Chloride	1.4	1.1	1
Dichlorotetrafluoroethane		3.3*	
Ethyl Chloride		1.2	
Trichlorofluoromethane	1	1.2	1
Dichloromethane		1.3	
Trichlorotrifluoroethane	3.7*	0.5*	0.2*
1,2-Dichloroethane	3.5*		
1,1,1-Trichloroethane	0.10	1	0.83
Benzene	2.6	0.87	0.8
Carbon Tetrachloride		1*	
Toluene	0.72	1	0.88
Tetrachloroethylene		1*	
Chlorobenzene		1	
Ethylbenzene	1.0*	1	1*
<i>m</i> -Xylene	0.45*	1.1	1
<i>o</i> -Xylene	0.6*	1	1*
4-Ethyltoluene	0.4*	1*	1*
1,3,5-Trimethylbenzene	1.4*	2.8*	1*
1,2,4-Trimethylbenzene		1	
<i>m</i> -Dichlorobenzene	9.9*	1	
<i>p</i> -Dichlorobenzene		1*	

Notes: 1. Blank entry indicates concentration below detection limits.

*Denotes that concentrations were ≤ 0.2 ppb.

2. Ratio of the average of 5 cans along the path to bicycle.

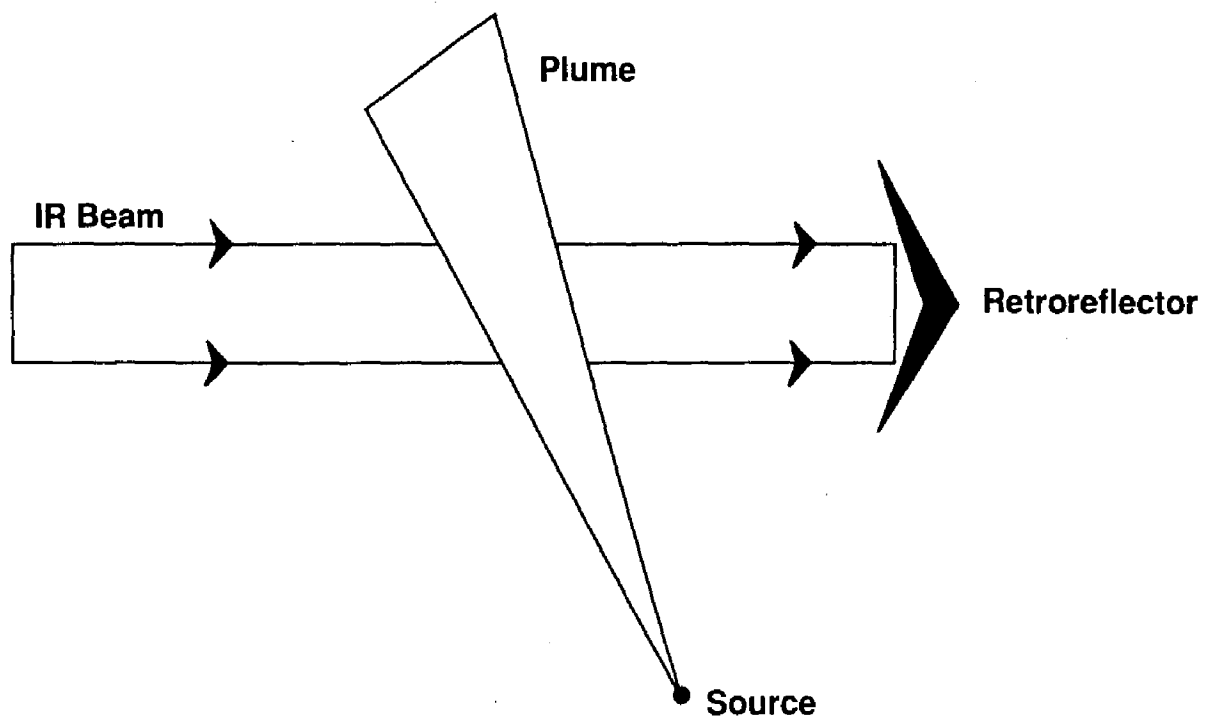


Figure 1. Plume/optical beam configuration.

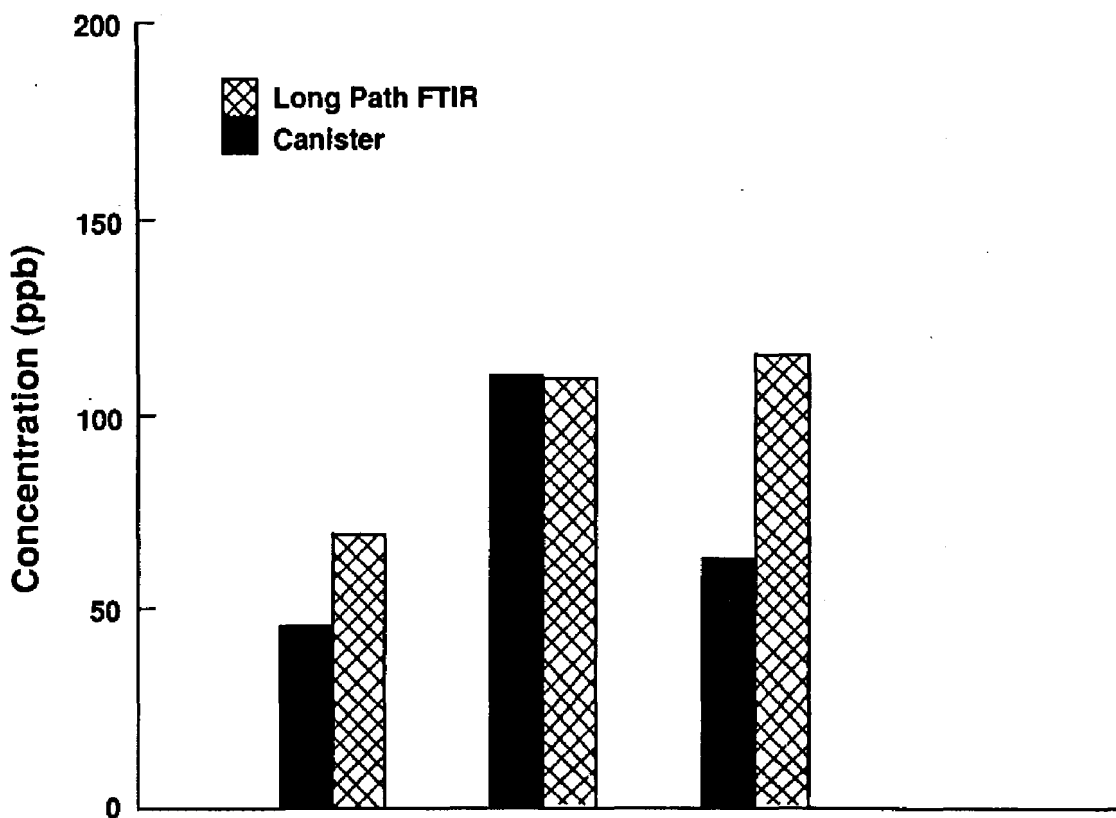


Figure 2. FTIR - canister comparison for chlorobenzene.

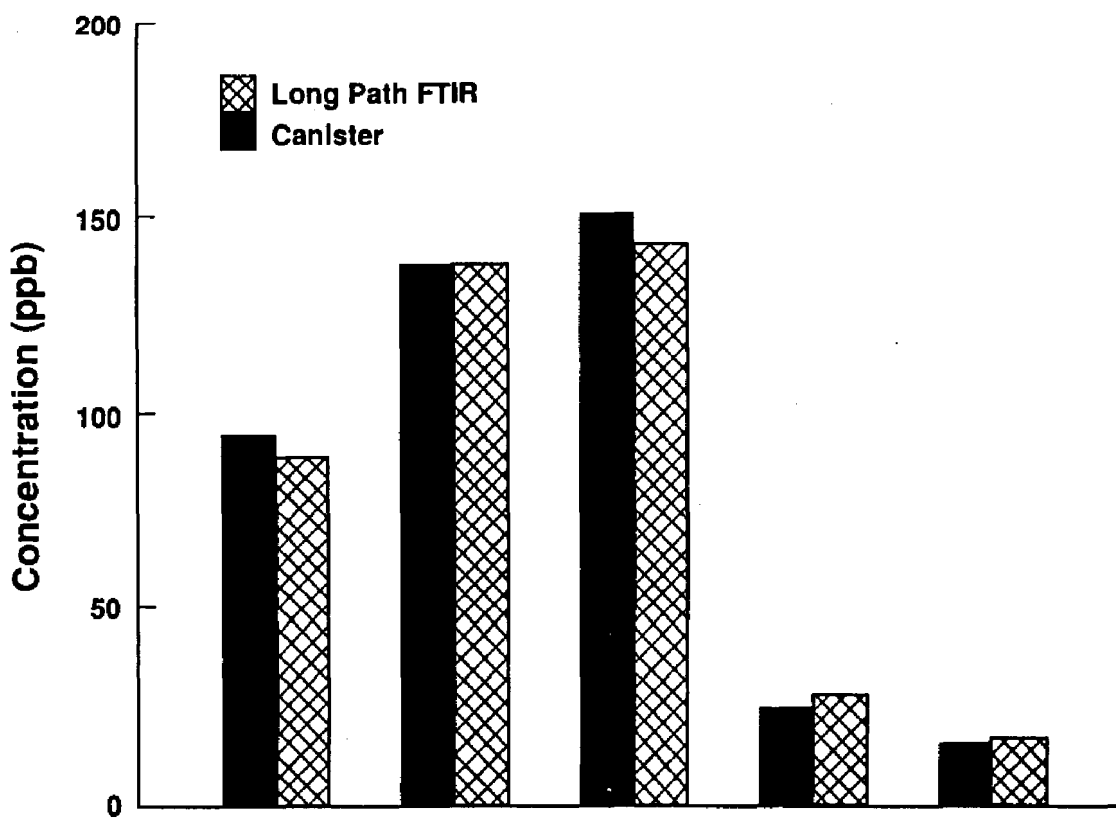


Figure 3. FTIR - Canister comparison for *p*-dichlorobenzene.

SHORT-TERM SEQUENTIAL CANISTER-BASED SAMPLING NEAR SUPERFUND SITES

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A commercially available, 14-port sequential canister sampler was used in a residential area of New Castle, Delaware, during July and August 1989 to automatically collect ambient air samples for 20 min at hourly intervals. The samples were subsequently returned to the laboratory and analyzed for 41 volatile organic compounds (VOCs) by gas chromatography (GC) with mass selective detection and flame ionization detection. The portable, battery-operated sampler is more easily deployed in the field than a GC system, yet it still allows collection of hourly samples so that short-term fluctuations in concentrations of VOCs in the ambient air can be monitored. These variations in concentrations would otherwise be averaged out by the collection of, for example, a 24-hr sample. The resultant hourly concentration data for a set of 25 VOCs was combined with wind direction and wind speed data to determine which local sources were impacting the site.

Introduction

State and local air monitoring agencies are often faced with the task of responding to a complaint from the public related to a persistent or noxious smell. To respond to such a complaint, the agency needs a means of locating the source. In the Delaware Superfund Innovative Technology Evaluation (SITE) study, a portable, battery-operated sampling unit was deployed to develop an ambient air data base for volatile organic compounds (VOCs) that was updated hourly at a sensitive receptor site, in this case the backyard of a residence located in Llangollen Estates near Superfund sites and not very far from industrial emission sources. The project goal was to interpret the temporal variations in VOC concentrations and wind direction (and speed) to identify local VOC emission sources.

Experimental

An automated, computer-controlled, 14-port sequential canister-based sampler¹ (SIS, Inc., Moscow, ID) and 6-liter SUMMA polished canisters (SIS, Inc.) were used to collect 18 ambient air samples at hourly intervals in a residential area of New Castle, Delaware. Purge/sample/pause times were programmed into the computer. Laboratory tests were performed to certify that the sequential sampler was not contaminated. The certification consisted of passing a mixture of VOCs at 10-ppbv levels through the canister-based sampler into a preconcentrator/gas chromatograph (GC) for analysis. The results of analysis were compared to the results obtained by passing the same sample directly into the GC. Table I shows the results expressed as a percentage difference referenced to the control results at each of three ports on the sampler. To further test the sampler, it was placed outside in the sun on a hot day and used to collect ambient air into a canister. Simultaneously, a canister equipped with a mass flow controller set to sample at the same flow rate as the sequential sampler was used to collect ambient air. The agreement as shown in Table II was excellent.

During the experiment in Delaware, the sampler was placed at the backyard site and programmed to allow for sampling every hour. Prior to the collection of each sample, all sample lines were automatically purged for 4 min with ambient air. Next, ambient air was collected for 22 min at a flow rate of 400 cm³/min, resulting in a total volume of 8.8 liters of sample collected in each canister. After sample collection, the sampler paused for 34 min before beginning the next purge/sample/pause cycle. Operation of the sampler was begun at 14:04 on July 25 and was completed at 07:46 on July 26, 1989. Wind speed and wind direction data were recorded every 15 min at a site approximately 1.6 km southeast of the residential area by using a portable, battery-operated meteorological data system (Climatronics, Bohemia, NY).

After sample collection, the canisters were returned to the laboratory for analysis of VOCs using an automated cryogenic preconcentration GC system with flame ionization and mass selective detectors (GC-FID/MSD). The peak areas of 25 of the most prevalent VOCs detected by flame ionization (Table III) were compared by using the Temporal Profile Analysis (TPA) technique² to determine which volatile compounds were correlated with each other. Wind direction and wind speed data were then used to calculate the trajectories of the air masses which moved across the site during and prior to the sampling periods.³

Results

Analysis results for the 18 samples indicated relatively low levels of VOCs at the residential site during most of the sampling period. However, significant increases in

concentrations of VOCs were observed at 1:30 a.m. and 5:30 a.m. on July 26. During these occurrences, *p*-dichlorobenzene, as measured by GC-MSD, increased from an undetectable level (<0.05 ppbv) at 12:30 a.m. to 5.2 ppbv at 1:30 a.m. and was again undetectable by 2:30 a.m. *para*-Dichlorobenzene then increased from an undetectable level at 4:30 a.m. to 14.0 ppbv at 5:30 a.m., and by 6:30 a.m. it was present at less than 0.1 ppbv. The TPA results indicate that a number of compounds were well correlated with *p*-dichlorobenzene during these occurrences. All of the VOCs in Table III with the exception of isoprene, 1,2,4-trimethylbenzene, and unknown 1 correlated strongly with each other, as indicated by a correlation coefficient of 0.85 or greater.

Plots of the trajectories of air masses during the hour prior to the concentration increases at 1:30 a.m. and 5:30 a.m. show that the air mass travelled to the sampling site from the south on both occasions. One of the trajectories is shown in Figure 1. Many industrial sources such as the Texaco refinery and Standard Chlorine are located approximately 4 km south of the residential area, and the compounds which increased may have been carried to the residential area from those industrial sources.

Conclusions

A battery-operated, portable sequential sampler was successfully operated in a residential community to collect a series of hourly ambient air samples. The data base of VOC concentrations versus hour was interpreted to give the emission mix apparently originating from a local source by using temporal profile analysis. The success of this and other recent, similar experiments implies that VOC emission sources near sensitive receptor sites can be characterized and located.

Acknowledgement

The authors wish to thank M. W. Holdren of Battelle Columbus Laboratories for analyzing the samples discussed in this paper.

Disclaimer

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Table I. Sample integrity test of sequential canister sampler

Compound	Difference, %*		
	Port 5	Port 9	Port 14
Freon 12	13.6	7.33	5.33
Methyl chloride	7.91	0.57	-4.70
Freon 114	3.72	-4.02	-9.13
Vinyl chloride	-3.62	-5.79	-7.48
Ethyl chloride	3.85	0.52	-1.46
Vinylidene chloride	2.72	1.28	-1.49
Dichloromethane	4.01	1.72	-2.14
Freon 113	3.98	2.65	-1.88
1,1-Dichloroethane	3.15	2.01	-1.91
cis-1,2-Dichloroethene	3.19	2.99	-0.62
Chloroform	1.63	1.85	0.69
1,2-Dichloroethane	2.73	2.20	0.22
Methyl chloroform	2.48	1.57	-0.66
Benzene	2.24	1.44	-0.45
Carbon tetrachloride	-3.62	-0.28	1.95
1,2-Dichloropropane	2.51	1.69	-0.97
Trichloroethene	3.59	3.05	1.05
1,1,2-Trichloroethane	2.12	3.16	0.98
Toluene	1.94	3.47	2.96
1,2-Dibromoethane	0.81	5.47	3.37
Tetrachloroethene	3.01	4.66	2.28
Chlorobenzene	3.08	6.16	4.68
Ethylbenzene	2.74	2.53	1.48
m,p-Xylene	2.06	3.91	3.32
Styrene	4.04	6.56	6.78
4-Ethyltoluene	3.95	8.06	8.90
1,3,5-Trimethylbenzene	3.95	10.3	10.6
1,2,4-Trimethylbenzene	5.39	9.23	11.3
p-Dichlorobenzene	14.2	18.2	24.3
o-Dichlorobenzene	14.2	15.7	19.1
1,2,4-Trichlorobenzene	16.8	25.8	36.4
Hexachlorobutadiene	3.13	6.60	16.2

*Difference was computed as (Port - control)/(control) * 100

Table II. Comparison of ambient air samples collected using the sequential canister sampler and a canister equipped with a mass flow controller

Compound	Concentration, ppbv	
	Port 5	Canister
Freon 12	3.42	3.44
Freon 11	9.07	9.49
1,1,1-Trichloroethane	0.22	0.23
Benzene	0.84	0.85
Carbon tetrachloride	0.15	0.16
Toluene	1.19	1.08
<i>m,p</i> -Xylene	0.55	0.52
4-Ethyltoluene	0.60	0.61
1,2,4-Trimethylbenzene	0.21	0.25

Table III. Twenty-five most prevalent compounds at a residential sampling site in New Castle, Delaware

Propane and propene	Hexane
Isobutane	Benzene
Unknown 1	3-Methylhexane
Butene	Heptane
<i>n</i> -Butane	Toluene
Isopentane	Unknown 3
<i>n</i> -Pentane	Chlorobenzene
Isoprene	<i>m,p</i> -Xylene
<i>trans</i> -2-Pentene	<i>o</i> -Xylene
2-Methyl-2-butene	1,2,4-Trimethylbenzene
Unknown 2	<i>p</i> -Dichlorobenzene
2-Methylpentane	Substituted benzene
3-Methylpentane	

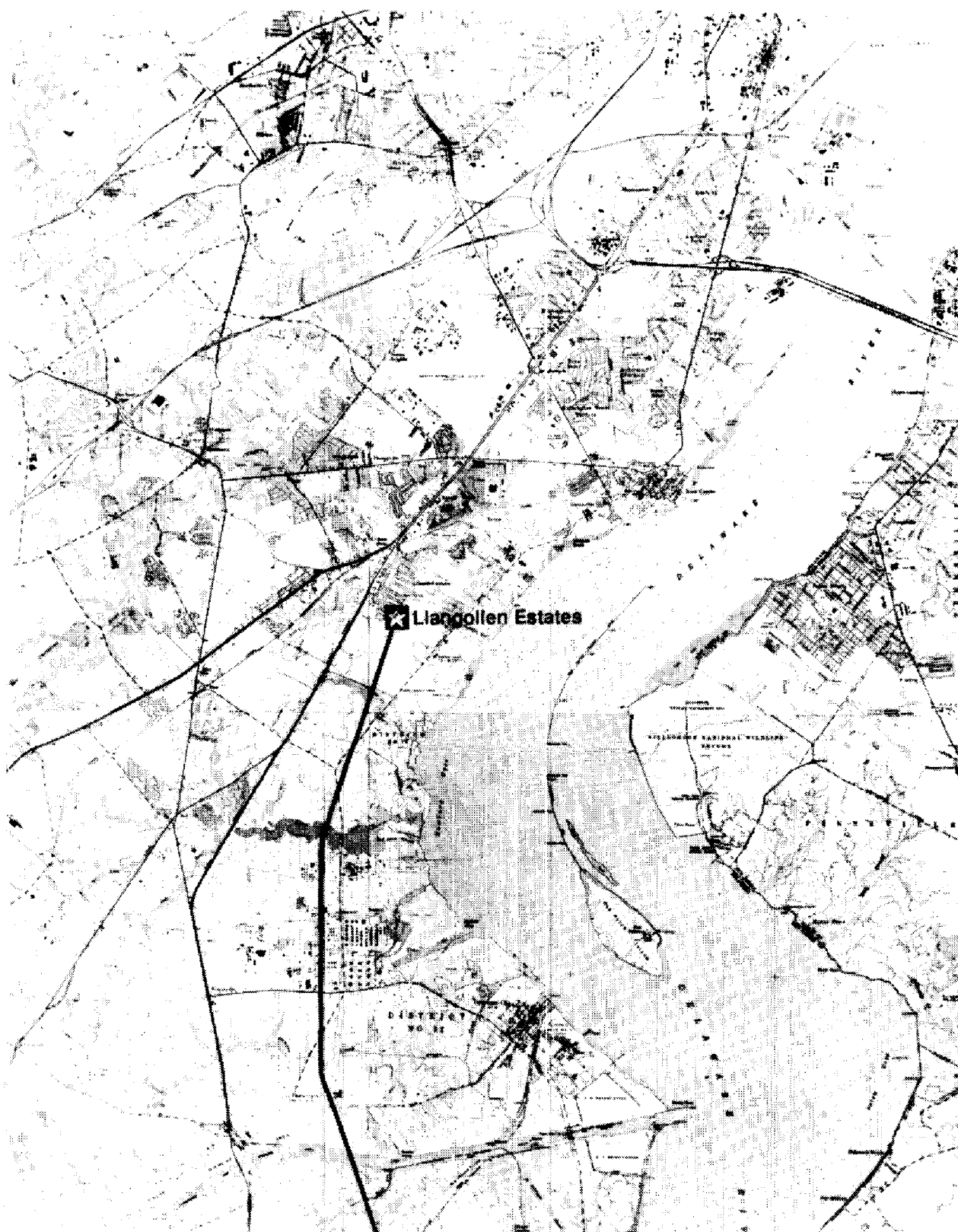


Figure 1. Trajectory of air mass prior to detection of high concentrations of VOCs at Llangollen Estates.

SPATIAL AND TEMPORAL CORRELATION OF WIND DIRECTION AND SPEED OVER A SMALL REGION

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During a recent field study in Delaware a set of wind direction and speed data was collected from four sites spread over about 10 km. An attempt was made to determine whether the data from two of these sites separated by 3 km show any correlation between the wind speed and direction. Although the back trajectories calculated from a subset of these look very similar, it is difficult to show a definite correlation between the two sets. The data show that when the wind speed is less than about 3 mph careful consideration must be given to its use for these calculations.

Introduction

During the Delaware study, a set of wind speed and direction data was taken at two stations separated by 3 km. These data were taken continuously as 15-min vector averages for a 10-day period. One of the sites was on top of a one-story building that was situated at the top of a small hill overlooking the Delaware River. The second was 3 km south at about the same elevation (perhaps 20 ft lower). This station overlooked the Delaware River also, and both were about one-half mile from it. A subset of the total data representing a continuous block of four days taken at both of these stations is used for the remainder of this discussion.

Results and Discussion

One way to present wind data is to plot wind roses, and these are shown for the two sites for the four-day period in Figure 1. These are plotted with 22.5° segments in azimuth and 5-percent increments radially. For these two stations, the calm periods represented about 5 and 15 percent of the total time. Other than giving some general information about the character of the winds, these diagrams do not appear to be too informative, however. They do not, for example, give the sequence of events of when the wind was coming from what direction and with what speed. These plots do show that the predominant winds for this period were from the two northerly quadrants at both stations. The distribution of the angle of the wind at P4 is significantly different than that at the substation. The implication is that if these sets of wind data are used for back trajectory calculations, differences in the air parcel paths should be expected.

For some of the experiments conducted in Delaware, an attempt was made to use the wind information to track the air parcel back from the instruments to an industrial complex. An implicit assumption in doing this is that if the wind speed and direction are measured at point A (the monitor), there is some confidence that this wind pattern is the same at point B (the source), a short distance away. It was hoped that these two data sets would allow that assumption to be tested, and the four-day back trajectories are shown in Figure 2. It should be pointed out that we were interested in trajectories going back in time for a few hours and not days; the four-day span is used to show the trajectories more clearly. These plots are on a scale of 1 to 2.5 million in order that the trajectory would fit on an 8½ × 11-in. sheet of paper; thus, the geographical area covered is quite large compared to the region we were interested in. Also, all the calculations were done by using vector addition or averages, and no scalar mathematics was used.

At first glance, these curves appear to be quite similar and to be correlated. Proving this is another matter, however. There are two sections to these curves; one is the lower, more or less horizontal section and the other, the vertical section. If the scale is kept in mind, the two lower sections are seen to diverge quite rapidly. Although there seem to be differences in the wind speed, the angular divergence predominates in this region of the trajectories, at least initially. The reverse is true for the vertical sections of the trajectories, where the wind directions appear to be in much better agreement.

This interpretation is borne out in Figure 3, which shows the geographical distance between the two trajectories as a function of time. This graph shows that the two trajectories diverge to about 70 miles over the first 24 hr, but then no further significant divergence occurs.

To further analyze this data set, use was made of the fact that these data points

are vectors and the dot product could supply useful information. The interpretation of the dot product is similar to that for the correlation coefficient used with scalar data.

The average wind speed for each pair of data points was calculated, and then the ratio of the magnitudes versus average wind speed was plotted. The plot is shown in Figure 4. Actually, this plot was done by sorting the data on average speed and then plotting it as a function of sequence number. This makes viewing the data clearer, but it should be noted that only 15 percent of the total data lies above 6 mph. There are two things to be noted about this curve. The first is that at less than about 3 mph the data are quite variable. If the wind speed were perfectly correlated, this plot should be a horizontal line with a value of 1. The second point to notice is that there seems to be a lower value to the data, even at higher speeds, that is different from 1. From the actual data this value is seen to be 1.6. The first point implies that, when the wind speed is less than about 3 mph, using the data for back trajectory calculations should be done only with the recognition that significant error may be present. The second point indicates that there may be something wrong with the instruments in that there is a constant bias between them. When the data for the trajectories are replotted after all the wind speeds from the substation are multiplied by the factor 1.6, as shown in Figure 5, the resulting coincidence is at first much better. Note, however, that the lower portion of the curves still diverges almost as much as it did in the original. If the trajectories are replotted by using only $2\frac{1}{2}$ days of the data, as shown in Figure 6, the vertical portions of the curves are in good agreement, and we do not have to invoke the problems of large instrumental bias. At this time it is felt that the instruments were functioning properly, and the differences in the first part of the curves are real.

This raises an interesting point, however, about the calibration of wind measurement devices. The only accepted procedure for calibrating the anemometer is to put it in a wind tunnel. Although portions of the instruments (electronics) can be checked in the field, there are apparently no field procedures to verify the accuracy of the entire system under field conditions. This is indeed a severe handicap.

The last graph, Figure 7, shows the cosine of the difference of the two wind directions plotted as a function of average wind speed. This should have a value of 1 if the two directions are colinear and a value of -1 if they are 180° apart. Again, the data is quite variable at wind speeds less than about 3 mph.

Conclusions

This data set implies that a lower limit exists for the use of wind information in the calculations of back trajectories. When the wind speed is less than about 3 mph, the assumption that a single data set holds for even a small region surrounding the site probably does not hold true.

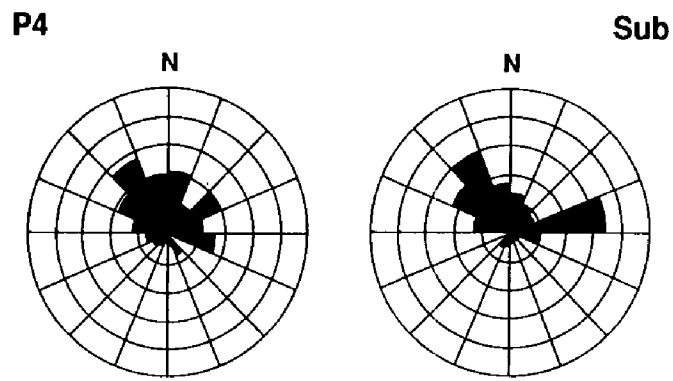


Figure 1. Wind roses P4 and substation.

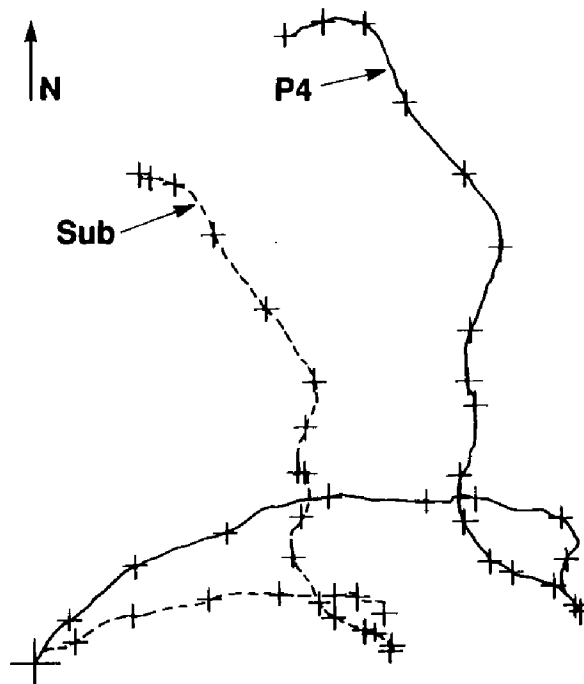


Figure 2. Four-day back trajectories.

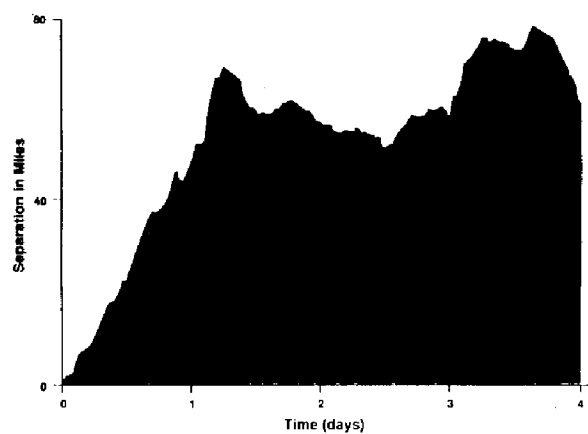


Figure 3. Separation distance versus time.

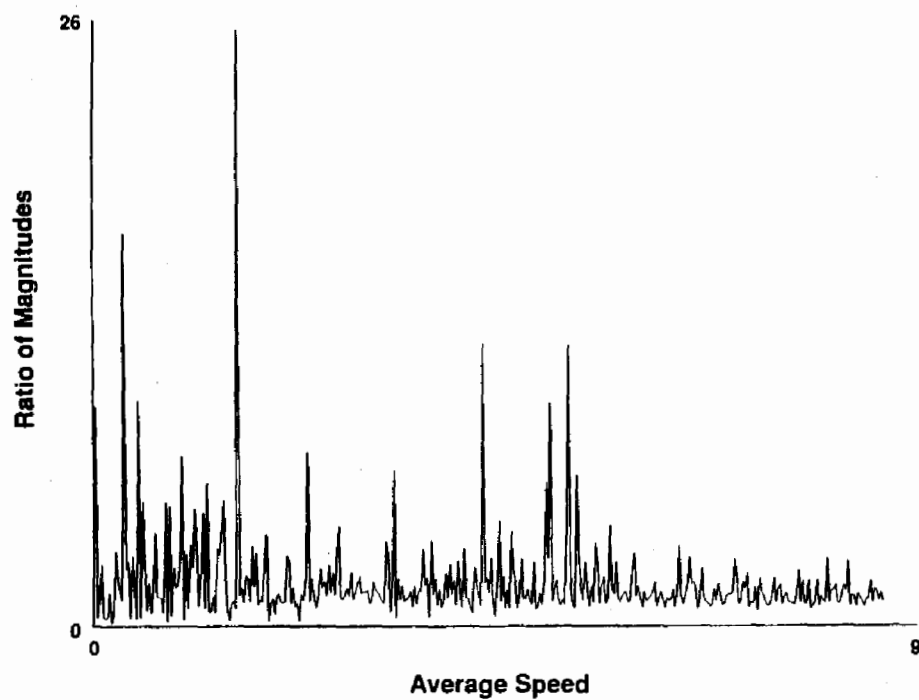


Figure 4. Ratio of magnitudes versus average speed.

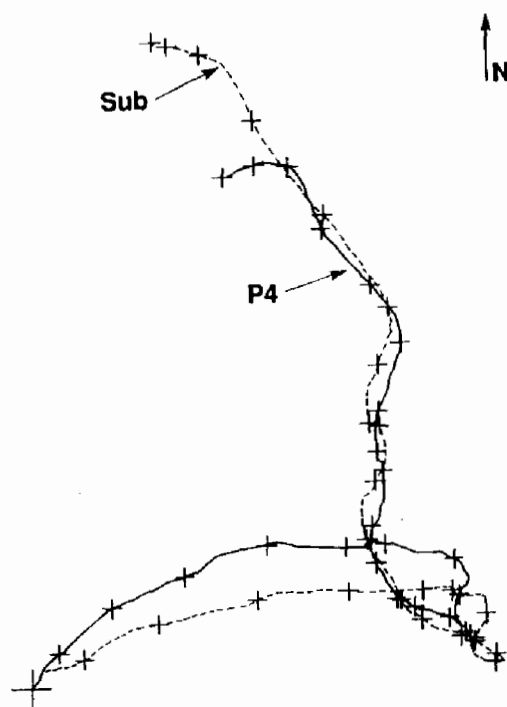


Figure 5. Four-day back trajectories (sub \times 1.6).

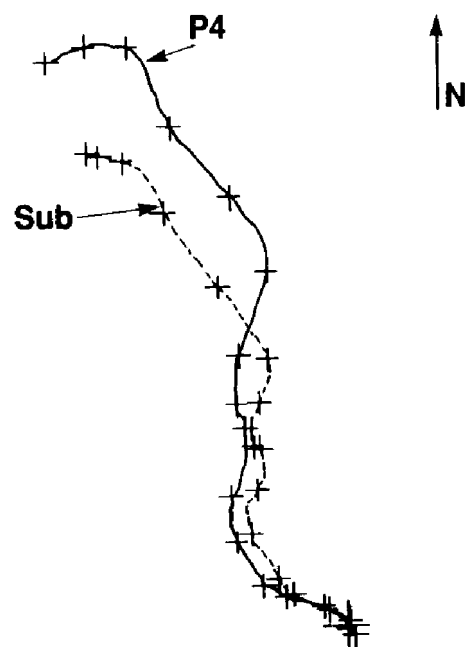


Figure 6. Back trajectories for 2½ days.

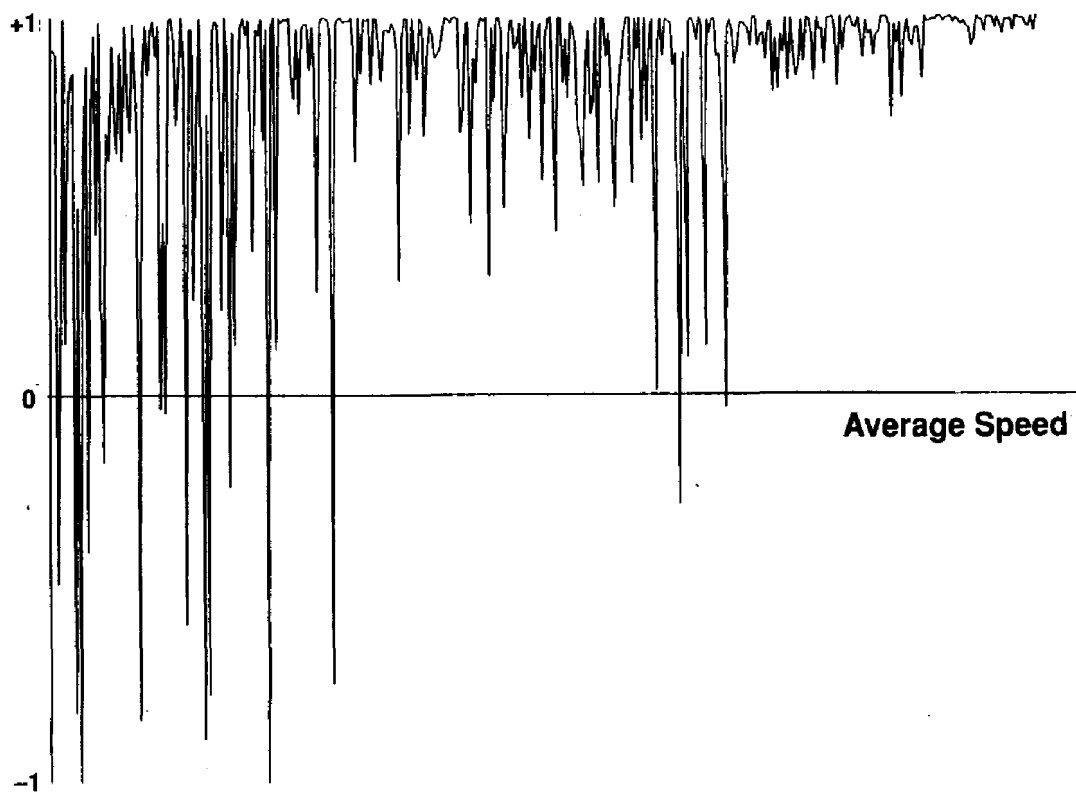


Figure 7. $\cos(\theta - \phi)$ versus average speed.

SPECIATION OF ORGANIC COMPONENTS OF MOBILE SOURCE EMISSIONS

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Both the evaporative and tailpipe emissions from mobile sources are complicated mixtures of organic and inorganic compounds. To get a better understanding of these emissions and to determine effects of fuel, vehicle and operating conditions on the emissions, speciation of the many, sometimes over 250, organic components is needed. This paper describes the four different gas chromatographic methods used to get the maximum speciation information. The methods for diluted emission samples collected in Tedlar bags are: Most of the compounds from C_4 to C_{12} are analyzed on a 60m DB-1 capillary column programmed from either -60°C or -50°C to about 180°C with a hydrogen flame ionization detector (FID); methane is analyzed on a molecular sieve-Poropak QS column at 30°C with an FID; $C_2 - C_3$ are analyzed with a silica gel column at 30°C with an FID; and the seven C_4 's are analyzed with a 0.19% picric acid on Graphpac at 43°C with an FID. GC methods have also been developed to analyze fuels including oxygenated compounds such methanol, ethanol, methyl tertiary butyl ether (MTBE) and ethyl tertiary butyl ether (ETBE), compounds used in alternative fuels.

INTRODUCTION

Gaseous hydrocarbon emissions from motor vehicles are of concern primarily because many of these hydrocarbons are oxidant precursors in atmospheric photochemical processes¹⁻⁴. These transportation related pollutants have been characterized as one of the most significant air pollution problems. In most Urban areas, the hydrocarbon emissions from mobile sources account for more than half of these precursors. Quantitative speciation of vehicle hydrocarbon emissions is needed, to elicit a better understanding of the Mobile Source contribution to this ozone (oxidant) nonattainment problem. Another area of interest for these analyses is the potential toxicity and carcinogenicity of the components in Mobile Source emissions⁵. Benzene and 1,3-butadiene, which are regarded as hazardous pollutants, are two examples of compounds found in large amounts in automobile exhaust. Accurate determination of these and other compounds are difficult because of the large numbers of similar compounds many of which coelute from gas chromatographic columns when analyzing vehicle emissions.

In the Mobile Sources Research Branch (MSERB) of the U.S. Environmental Protection Agency several different gas chromatographic (GC) methods are used to obtain the maximum speciation information of vehicle emissions. Two different gas chromatographs are currently in use in this laboratory to analyze for hydrocarbons. The first instrument has been modified into two sections. In the first section an aliquot of the collected emissions sample is taken to measure the compounds methane, ethane, ethylene, and acetylene. A modification recently made to this section requires two samples for analysis but extends the analysis so that propane and propylene are also measured. The second section of this instrument is used for the detailed analysis of the C₃ to C₁₃ hydrocarbons. The second instrument is configured into four sections and four samples are, therefore, required for complete speciation analysis. In one section of this instrument only Methane is measured. Ethane, ethylene, acetylene, propane, and propylene are measured in another section of this instrument. The seven C₄'s that are found in Mobile Source emissions are measured in the third section⁶. The detailed analysis of the C₄ to C₁₃ hydrocarbons is done in the fourth section⁷.

Gasoline and other fuels are run on another GC instrument similar to that used for the speciation of the C₄ to C₁₃ hydrocarbons. Liquid samples are introduced to the separating columns by flash vaporizing the sample in a heated injection port on the GC. In addition, liquid samples can be analyzed by vaporizing an aliquot of the sample into a heated manifold which is continually being purged with a metered amount of zero grade air.

Gas Chromatography/ Mass Spectrometry is used for positive identification of the peaks and to determine if peaks contain more than one component and whenever possible identify the components and their compositional ratios.

Another gas chromatographic analytical system is used to

analyze samples for oxygenates such as ethanol, and methyl tertiary butyl ether (MTBE) when alternative fuels are tested. This system involves cryogenically concentrating an aliquot of the sample and analyzing the ethanol and MTBE through a dual column arrangement with an additional cryofocusing step⁸. Methanol is measured with another gas chromatograph since emissions samples known to contain methanol are pumped through water and then an aliquot of the water is taken for analysis.

The carbonyl compounds which may be present in vehicle emissions samples, such as aldehydes and ketones, are collected on cartridges containing silica gel treated with

2,4- dinitrophenylhydrazine. The derivatized aldehydes and ketones are then analyzed by high performance liquid chromatography (HPLC).

EXPERIMENTAL

Sampling

Gas samples were collected in Tedlar bags (E.I. du Pont de Nemours and Co. Wilmington, Del.) from the Constant Volume System (CVS) and evaporative emissions test cell. New bags are flushed four to five times with zero air to eliminate contamination problems.

Sample Introduction

Two different methods are used to introduce the samples into the chromatographic system from the bags. One method involves the use of a sample loop constructed of clean chromatographic grade stainless steel tubing in 1 ft., 5 ft., or 10 ft. lengths and 1/8 OD. The loops are coiled to fit inside a controlled temperature sample housing unit or to fit inside the gas chromatograph. The loop has been prepared for sample analysis by flushing it with methylene chloride and then dried with zero grade air prior to use.

The other method used for sample introduction involves the use of a hydrocarbon trapping system consisting of a stainless steel tube 6 in x 1/8 in OD packed with 4 in. of untreated glass wool. This trapping system can be used to analyze low concentrations of mobile sources exhaust. Sample collection volumes of up to 1500 cm³ have been used with this trapping system. This trap extended the detection limits for most hydrocarbons to the 15.0 parts per trillion carbon (pptrC) level.

A Nutech Model 320 controller (Nutech Inc. Durham, N.C.) maintains concentration and desorption temperatures in the individually controlled traps for the C₂ to C₃, C₄'s, and C₄ to C₁₃ analyses and heats the 1/16 OD stainless steel transfer lines. The traps and all the heated lines are wrapped with insulation tape. The transfer lines and Seiscor 6-port switching valves are maintained at 120°C while the Nutech controller holds the sample loop at -170°C with liquid nitrogen for the C₂ and C₃ concentrations, -155°C for the C₄'s, and -135°C for the C₄ to C₁₃ concentration. During the C₄ to C₁₃ analyses the trap is backflushed with helium at a trap temperature of 150°C.

Gas Chromatographic Methods

The two gas chromatographic analytical systems that are currently in use in this laboratory to analyze for hydrocarbons are a Hewlett Packard model 5880 and a Perkin-Elmer model Sigma 2000. Both GC systems use the same basic methodology but with different columns or slightly different oven temperature programming parameters due to the basic differences in the instruments physical configuration. Both GC systems utilize a flame ionization detector (FID) and transfer raw data to a PC-AT or compatible computer where the data is verified. Many of the same samples are analyzed by both systems in order to maintain quality control/quality assurance of our methods.

The C_1 to C_4 analytical procedure, shown in Figure 1, is run on the Hewlett Packard GC. Methane is measured by directing a 1 cm^3 aliquot of the bag to flow through a 6 ft. x $1/8$ in. o.d. stainless steel column packed with 60/80 mesh 13x Molecular Sieve. The column is operated at ambient with a $30\text{ cm}^3/\text{min}$ helium carrier flow. Ethane, ethylene acetylene, propane and propylene (C_2 to C_3) are analyzed by taking a 5 cm^3 aliquot of the bag and directing the sample to a 6 ft. x $1/8$ in. OD stainless steel column packed with 40/60 mesh type 58 Silica Gel. The column is operated at ambient with a $30\text{ cm}^3/\text{min}$ helium carrier flow. The C_4 hydrocarbons, iso-butane, n-butane, 1-butene, isobutylene, 1,3-butadiene, cis-2-butene, and trans-2-butene are separated on a 9 ft x $1/16$ in. OD teflon coated stainless steel column packed with 0.19% picric acid on 80/100 mesh Graphpac (Altech Assoc. Inc. Waukegan, Rd, Deerfield Ill.). The column is operated isothermally at 43°C with a $30\text{ cm}^3/\text{min}$ helium carrier flow.

The C_1 to C_2 hydrocarbons are analyzed with the Perkin Elmer GC as shown in Figure 2. A 10 cm^3 sample is directed through a 6 ft x $1/8$ in. OD stainless steel column packed with 40/60 mesh Poropak Q/QS and a 6 ft x $1/8$ in OD stainless steel column packed with 40/60 mesh type 58 Silica Gel. The column is operated at ambient with a $30\text{ cm}^3/\text{min}$ helium carrier flow. After 16 min the columns are backflushed to remove the higher molecular weight hydrocarbons.

A recent modification to the C_1 to C_2 analytical system that allows for the measurement of propane and propylene is shown in Figure 3. The main differences between the C_1 and C_2 analytical method and the C_1 to C_3 method is that a 6 ft x $1/8$ in. OD stainless steel column containing 60/80 mesh Molecular Sieve 13x is connected in series with the Poropak Q/QS column and that two samples are required for analysis. Methane is measured first by the Molecular Sieve/Poropak Q/QS columns and then the system is backflushed so that the second sample can be analyzed for the C_2 and C_3 compounds with the column containing Silica Gel.

The analytical systems used to do the C_2 or C_3 to C_{12} or C_{13} separations are shown in Figure 4, using the Perkin -Elmer GC, and in Figure 5, using the Hewlett Packard GC. Both GC's use a 60 meter x 0.32 mm ID fused silica capillary column to separate the relatively higher molecular weight hydrocarbons. The capillary column is coated with a 1.0 μm film thickness bonded methyl silicone liquid phase (DB-1, J&W Scientific. Folsom

Calif.) The oven temperature programming parameters are as follows:

Initial oven temperature:	-60°C
Hold at initial temperature:	6.5 min.
Oven temperature programming rate 1:	30°C/min. to -45°C.
Oven temperature programming rate 2:	6°C/min.
Final oven temperature:	175°C.
Detector temperature:	225°C.

Ethanol and MTBE are analyzed on a separate GC system shown in Figure 6. An aliquot from a bag sample is cryogenically concentrated at -155°C and then desorbed at 150°C. The sample is directed first into a 7 ft x 1/8 in. OD teflon column packed with 15% 1,2,3-tris cyanoethoxy- propane (TCEP) on 80/100 mesh firebrick with hydrogen as the carrier gas at a flow rate of 5.0 cm³/min. After the light hydrocarbons are vented (0.2 to 0.3 min) the column is backflushed to the head of another column where the sample is cryofocused with liquid CO₂. The alcohols and MTBE are then analyzed with a 25 meter x 0.53 mm ID fused silica capillary column coated with a 5.0 um film thickness methyl silicone bonded liquid phase. The columns are operated isothermally at 60°C and the detector temperature is set at 200°C.

Methanol is analyzed with a separate analytical system. This method requires that methanol be collected in water. The automobile exhaust sample is pumped through two impingers connected in series in order to trap the methanol in the water. A 1.0 ul aliquot of the water in the impinger is then analyzed by gas chromatography. The column used to separate the methanol from the water is a 25 m x 0.53 mm ID fused silica capillary column coated with a 5.0u film thickness methyl silicane bonded liquid phase. The carrier gas is helium with a flow rate of 20 cm³/min. The injection port temperature is 118°C, the detector temperature is 150°C and the oven temperature is at 100°C.

Calibration of systems

Both the oxygenate and detailed hydrocarbon analyses are calibrated by external standard methods. The C₂ to C₁₂ hydrocarbon analysis is calibrated by using a cylinder containing 16 hydrocarbons ranging from C₂ to C₁₁. Individual hydrocarbons are also analyzed by injecting the hydrocarbons into a Tedlar bag using the apparatus shown in Figure 7 to verify each component in the calibration cylinder as well as to confirm identifications made by GC/MS. Ultra zero grade air is swept through the injector where the hydrocarbons and oxygenates are flash vaporized at 150°C into an evacuated Tedlar bag. The calibration mix undergoes the same analysis as the unknown sample. The area counts of the standards are compared to the area counts of the unknown to calculate concentrations of the unknowns. Weekly calibrations are performed on each instrument, with at least five consecutive analyses to calculate precision and check for instrument drift. Daily span checks are compared to the control chart to ensure that the instrument is operating within the control limits on any given day. If the daily span checks are more than two standard deviations from the mean of the weekly calibrations then a second span check is performed. Corrective action is taken if the second check is also out of

control. The first out of control check is treated as an anomaly if the second check is within the control limits.

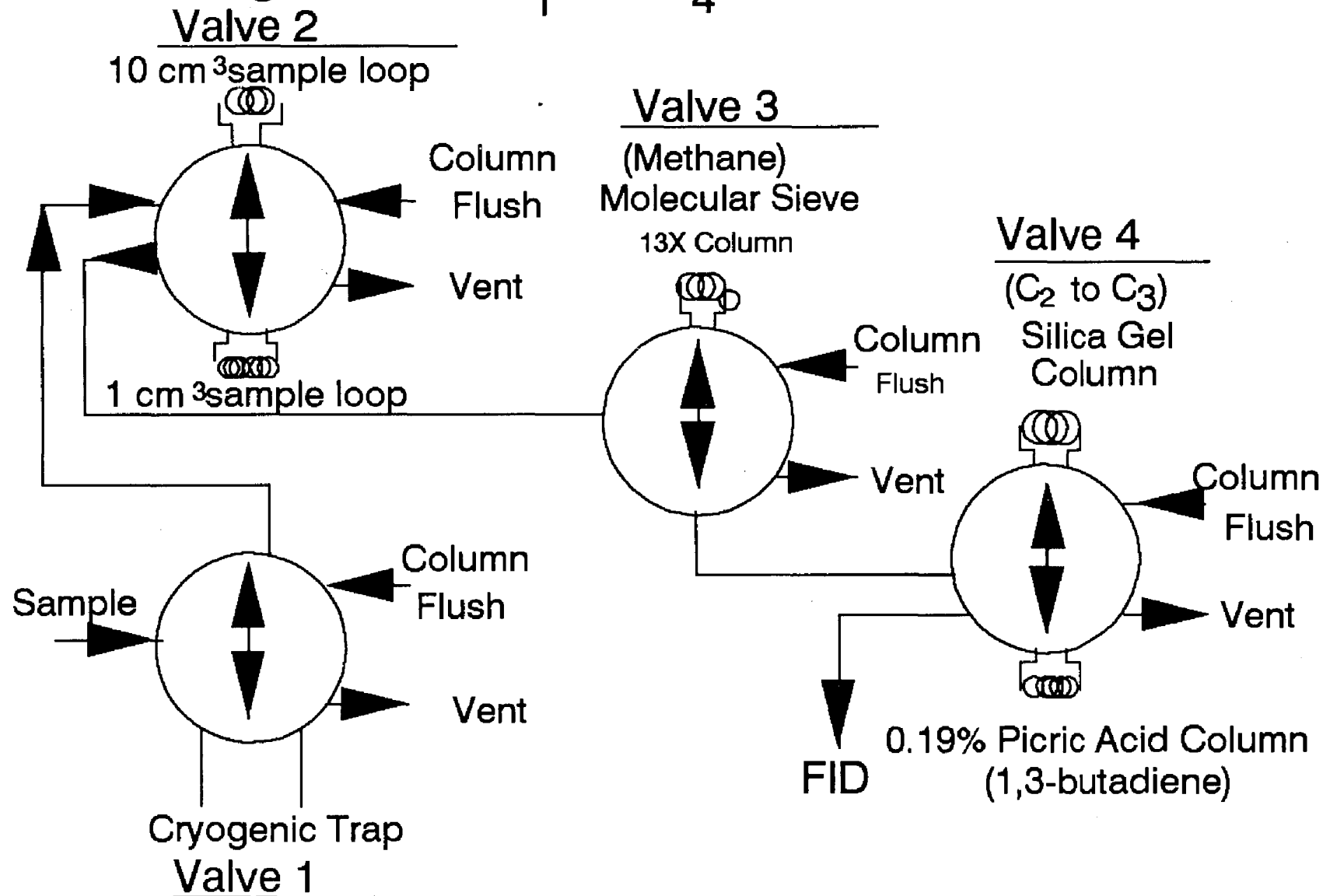
SUMMARY

Several GC methods have been described that permit maximum speciation of mobile source emissions. These methods entail the separation of the C₁ to C₁₃ hydrocarbons as well as the separation of oxygenate fuel additives such as methanol, ethanol, and MTBE. These methods are applicable to the analyses of diluted exhaust and evaporative emissions. In addition, with the use of cryogenic concentrating traps the limits of detection can be lowered to the low ppbC levels required for ambient air analysis. Gasoline, other fuels and pure liquid compounds are, also, analyzed by these methods using either direct liquid injection or by vaporization of the liquid into a heated and zero air purged manifold that is connected to a bag.

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Figure 1. C_1 to C_4 Analytical System



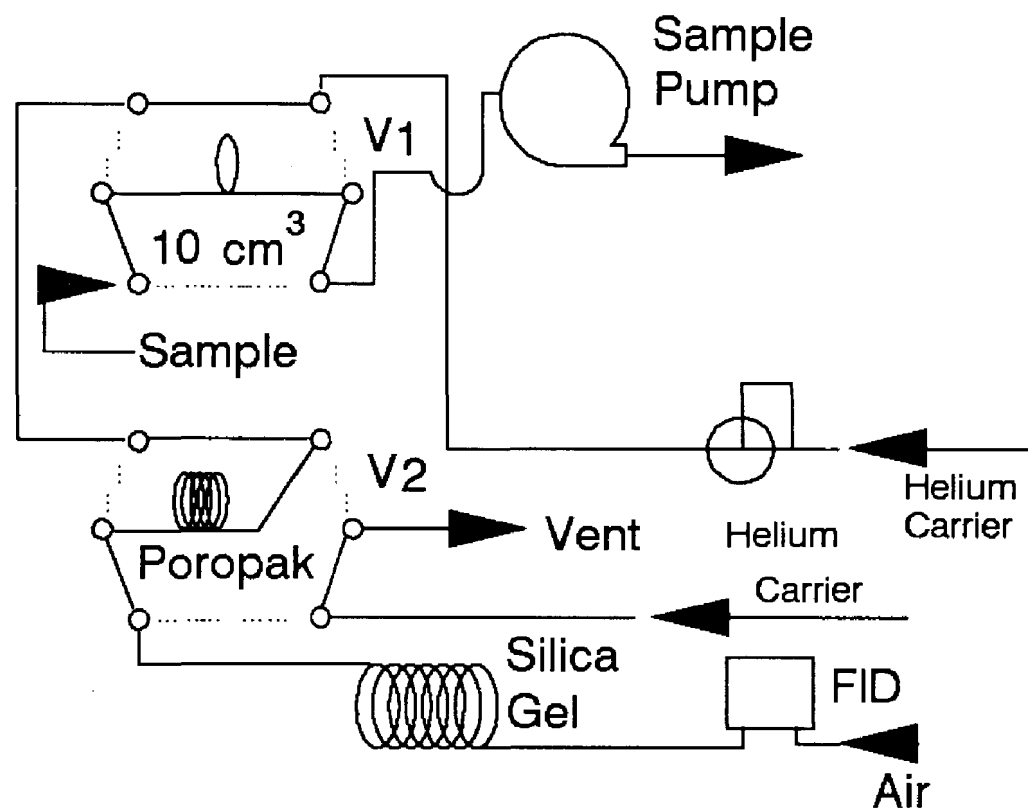


Figure 2. C_1 to C_2 Hydrocarbon Analysis

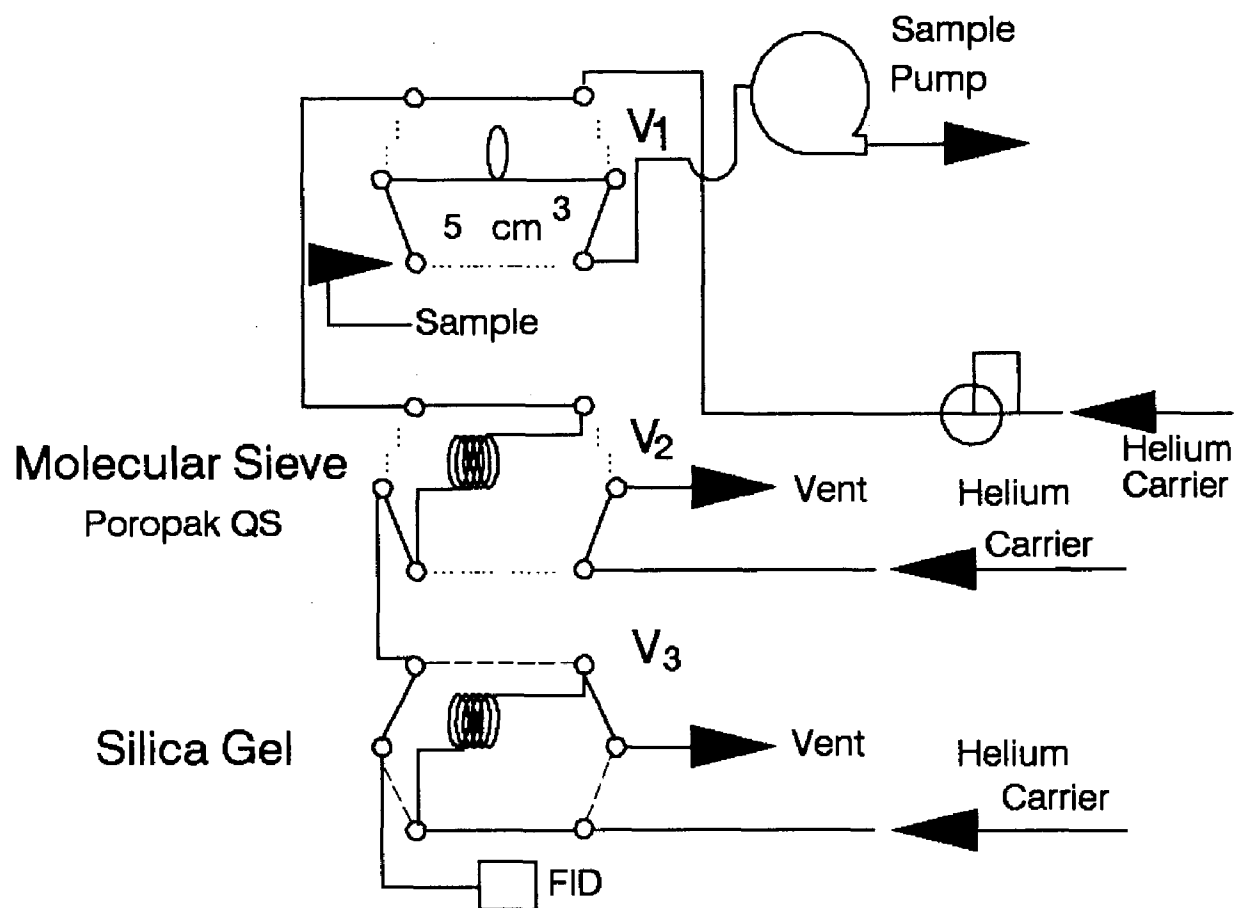


Figure 3. C_1 to C_3 Hydrocarbon Analysis

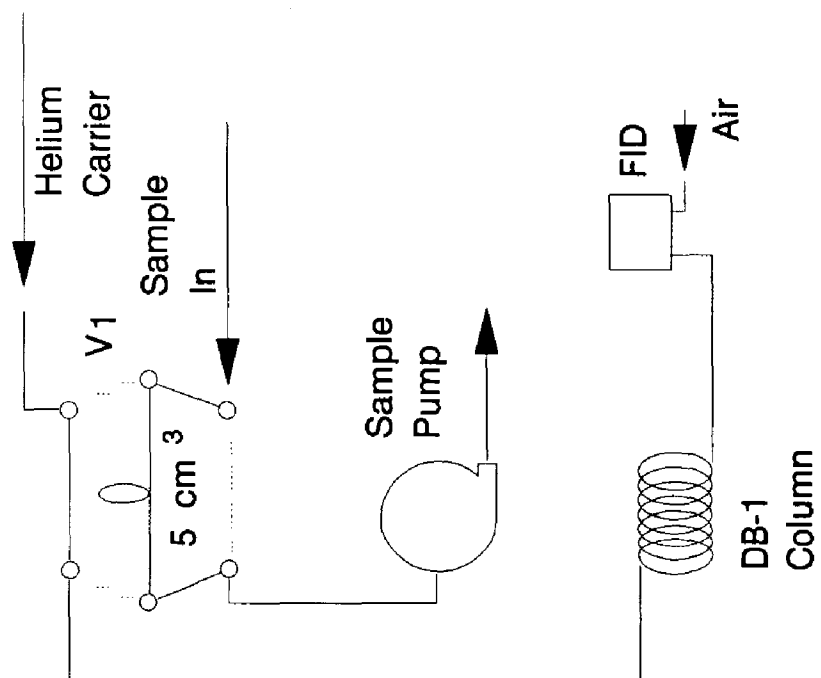


Figure 4. C_3 to C_{12} Hydrocarbon Analysis

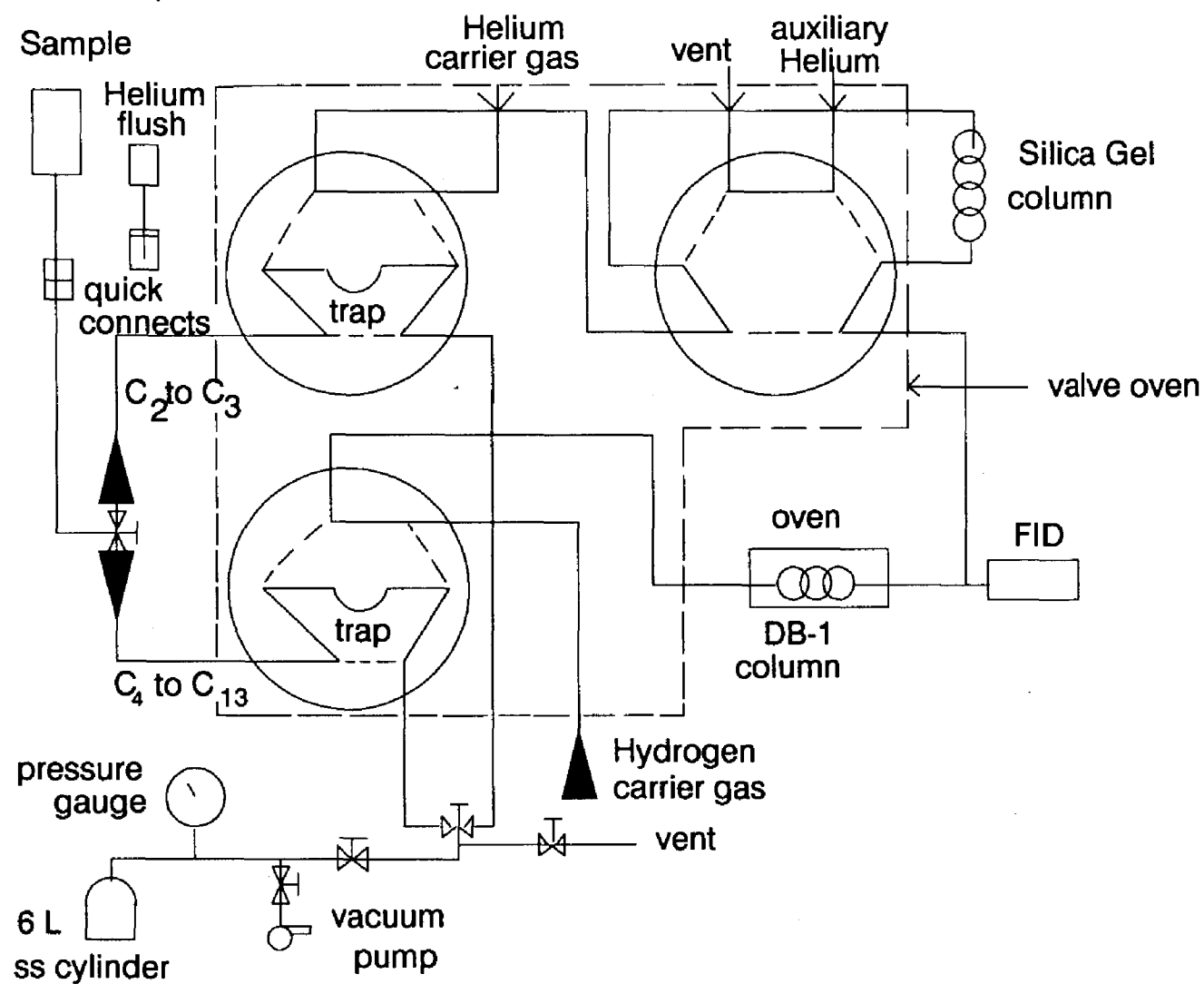


Figure 5. C_2 to C_{13} Hydrocarbon Analysis

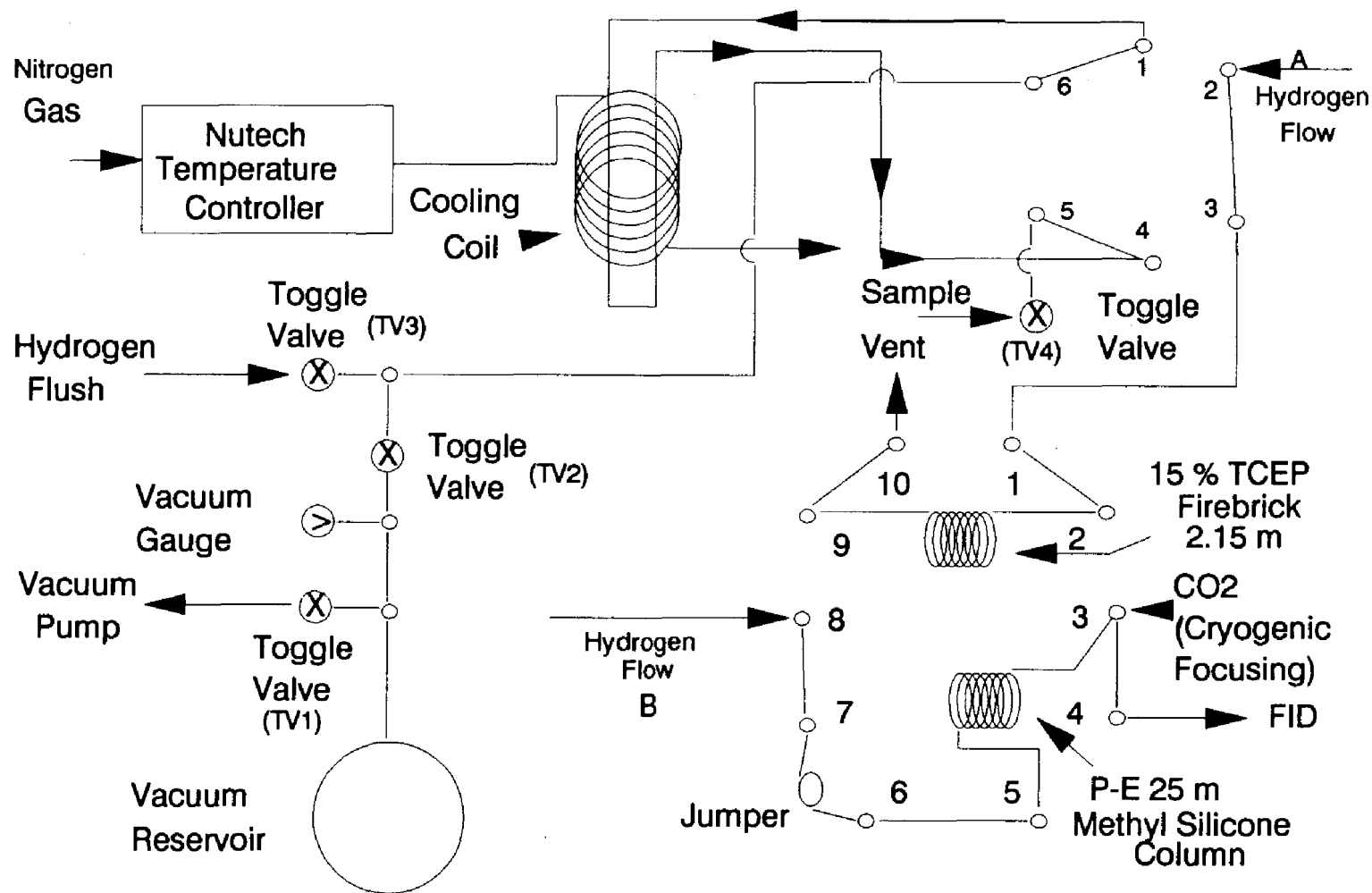


Figure 6. ETOH-MTBE Analytical System

Zero Grade Air

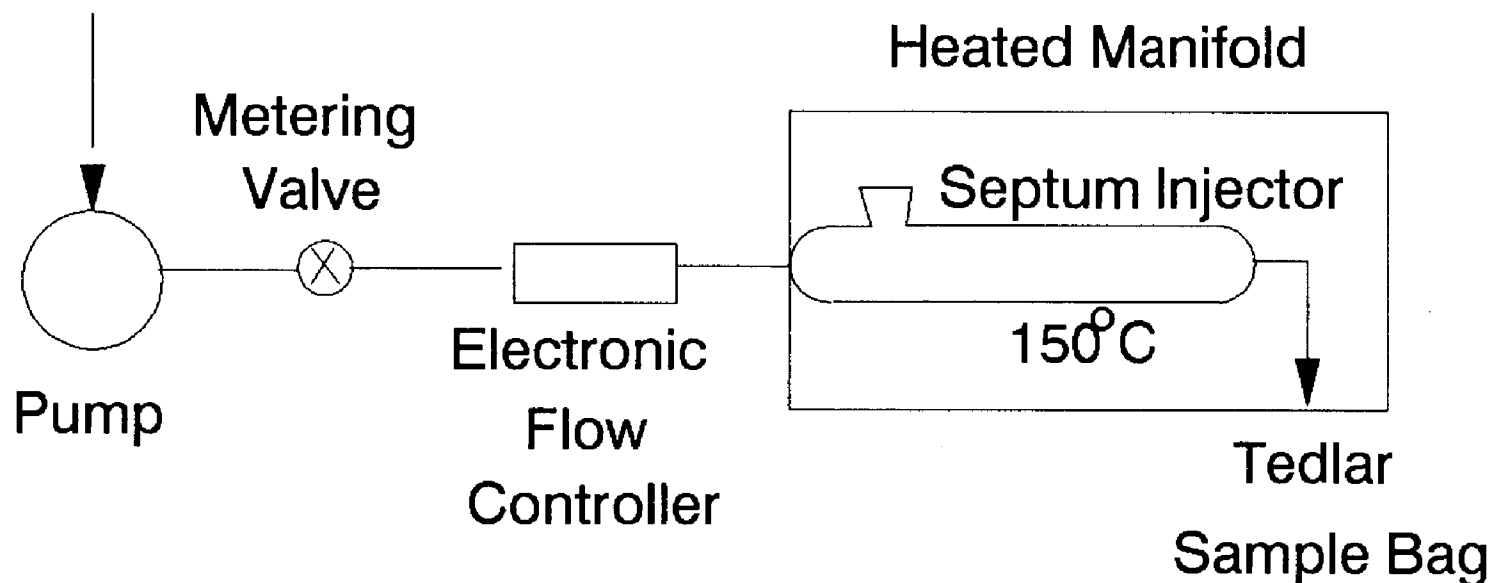


Figure 7. Heated Manifold for the Preparation of Calibration Mixes and Standards

COMPARISON OF DATA FROM A FOURIER TRANSFORM INFRARED AUTOMOTIVE
EMISSIONS SAMPLING AND ANALYSIS SYSTEM WITH THOSE OBTAINED FROM
CONVENTIONAL AUTOMOTIVE EMISSIONS ANALYTICAL INSTRUMENTATION

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Comparisons were made of a Mattson Fourier transform infrared spectroscopy based Real time Automotive Emissions Analyzer (REA) and classical analytical techniques. Data from the REA for CO, CO₂, and NO_x were compared to both integrated real time and bag results from conventional emissions analysis instrumentation. REA formaldehyde data were compared to results from the DNPH derivatization/LC technique. REA methanol data were compared with GC analysis of samples collected in water impingers. The exhaust emissions from automobiles fueled with gasoline, methanol, and methanol blends were analyzed as well as calibration mixes. The REA also allowed the acquisition of data on the emission composition of a variety of other compounds such as N₂O and NO. Generally good agreement was obtained between the REA results and those from the established techniques.

Introduction

The real time analysis of automotive emissions for regulated and unregulated emissions has received increased interest in recent years, especially with regard to alternatively fueled vehicles. Several research groups have developed FTIR based real time analysis systems recently.¹²³⁴ A FTIR based real time automotive emissions analysis system has been acquired and emissions data obtained from it have been compared to those obtained from conventional analytical instrumentation.

Experimental

All FTIR real time data were collected on the Mattson Instruments (Madison, WI) REA (real time emissions analyzer). The REA consists of a Mattson Nova Cygni 120 spectrometer, Masscomp 5300 computer and proprietary software developed by Ford Research Labs and Mattson Instruments. The sample flows through a 21.75 meter variable pathlength Wilkes gas cell made by Foxboro. Spectra are taken at 0.25 cm⁻¹ resolution, transformed and concentrations calculated such that concentration values are produced once every 3 seconds for approximately 22 selected compounds. Below is a listing of currently available compounds.

Table I. Possible Compounds from the REA.

<u>Hydrocarbons</u>	<u>Inorganics</u>	<u>Oxygenates</u>	<u>Others</u>
Methane	Carbon Monoxide	Formaldehyde	Ozone
Ethane	Carbon Dioxide	Acetaldehyde	Carbonyl Sulfide
Ethylene	Water	Methanol	Hydrogen Chloride
Acetylene	Nitric Oxide	Ethanol	Hydrogen Cyanide
Propane	Nitrogen Dioxide	Ketene	Ammonia
Propylene	Nitrous Oxide	Formic Acid	Sulfur Dioxide
1,3-Butadiene	Nitrous Acid		Carbon tetra-
i-Butylene	Nitric Acid		Chloride
trans-2-Butene			
i-Octane			

These concentration data were transferred to an IBM-AT computer where they are averaged and summarized for each bag of the driving cycle using Lotus macros and Pascal programs written in-house. A Horiba CVS (constant volume sampling) system supplied the diluted automotive exhaust samples. Approximately 70 standard FTP driving cycles (UDDS) were performed to produce the automotive emissions data. A 1988 GM flex fueled Corsica was operated on M0, M25, M50, M85, and M100 methanol fuel at 40, 75, and 90F for these FTP cycles. Conventional analysis data of CO₂, CO, and NO_x were acquired from the CVS analyzers. A real time data acquisition system operated on an IBM-AT computer by Data Translation Notebook (DTN) provided 1 second time resolved data from the CVS analyzers. Formaldehyde analysis was performed by the LC-DNPH method described by Tejada.⁵ Methanol analysis was performed by the GC-impinger technique.⁶ Bag samples were taken from the CVS system in Tedlar bags and analyzed after the test was completed. The general layout of the testing facility and sample collection has been described elsewhere.⁷

Discussion

Comparisons of the REA results show generally good agreement with those from the conventional analysis instrumentation. Specific comparisons are in the following table. Ratio averages for Bags 1, 2, and 3 are listed in descending order for each compound.

Table II. Ratio Comparisons REA vs Conventional Analysis

<u>DTN RT/ CVS</u>	<u>REA RT/ CVS</u>	<u>REA TN/ CVS</u>	<u>REA CVS/ CVS</u>
Carbon dioxide			
1.202(.028)	1.007(.042)	1.076(.076)	1.023(.079)
1.023(.015)	1.033(.059)	1.035(.104)	0.984(.091)
1.028(.018)	1.021(.055)	1.025(.088)	1.035(.086)
Carbon monoxide			
1.069(.041)	0.981(.096)	0.975(.126)	0.961(.120)
1.030(.056)	0.987(.117)	1.065(.158)	1.133(.204)
1.033(.087)	1.030(.141)	0.915(.300)	1.035(.233)
Nitrogen oxides			
0.996(.077)	1.088(.051)	1.035(.136)	1.033(.143)
1.036(.197)	1.042(.144)	1.222(.215)	1.063(.293)
1.025(.104)	1.063(.078)	1.019(.199)	1.057(.181)
Methanol			
	<u>REA RT/ LC</u>	<u>REA TN/ LC</u>	<u>REA CVS/ LC</u>
	1.035(.094)	1.021(.148)	0.984(.136)
	1.055(.285)	0.818(.315)	0.919(.377)
	0.771(.213)	0.764(.377)	0.713(.212)
Formaldehyde			
	1.088(.127)	0.987(.165)	0.972(.297)
	1.086(.180)	1.033(.230)	1.028(.205)
	0.984(.253)	0.997(.260)	1.051(.189)

The above carbon dioxide data show excellent agreement of the REA with the CVS analyzer for all three bags, both for the integrated real time analysis as well as the tunnel (TN) and CVS bag analysis. The carbon monoxide data and the oxides of nitrogen data also show excellent agreement for all the bag comparisons. The REA methanol data shows excellent agreement with the GC data for all the Bag 1 data, but Bag 2 and 3 data do not agree as well. This degree of disagreement can be attributed to the lower concentrations of methanol (0 to 10 ppm) found in Bags 2 and 3. Similarly, the formaldehyde data shows excellent agreement for the Bag 1 data, but Bags 2 and 3 data do not agree as well. Again, this can be attributed to lower concentrations in Bags 2 and 3 (10 to 200 ppb) than in Bag 1 (200 to 1500 ppb).

The REA also has the potential for modal analysis. Fig 1 shows how well the REA concentration trace for CO₂ compares with the DTN trace. As can be seen in the figure, concentration increases and decreases compare well. However, the peak concentrations in the REA trace are not as high and the low concentrations are not as low. This is due to the 5 L volume of the cell and the 25 L/min flow rate which combines for an approximately 10 second sample residence time in the cell. An

example of how modal analysis can be used is seen in Fig. 2. The CO concentration can be seen to greatly decrease at approximately the two minute mark, indicating the warming up of the car engine and the "lighting off" of the catalyst. As can be seen, the vast majority of formaldehyde and methanol in Bag 1 is produced in these first two minutes. Superimposing the driving trace upon the concentration trace in Fig 2, the effect of the rapid accelerations and decelerations have upon the emission concentrations can be seen.

Conclusions

The REA results have been shown to compare well with those obtained from conventional automotive emissions instrumentation for the compounds thus far studied. Additional compounds need to be studied and the potential for modal analysis fully explored.

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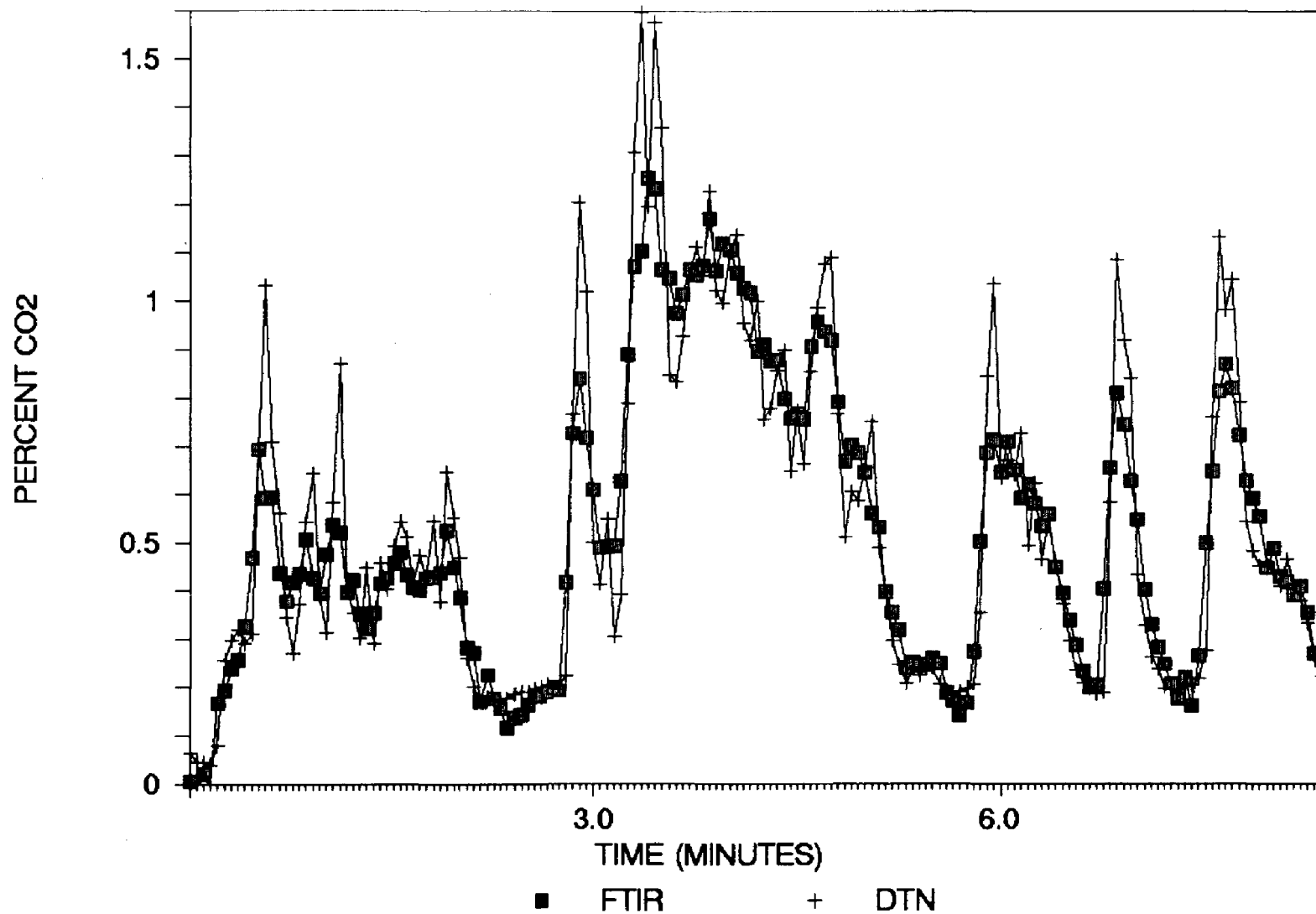


Figure 1. REA and DTN Real Time Trace
CO2 Bag 1 of FTP

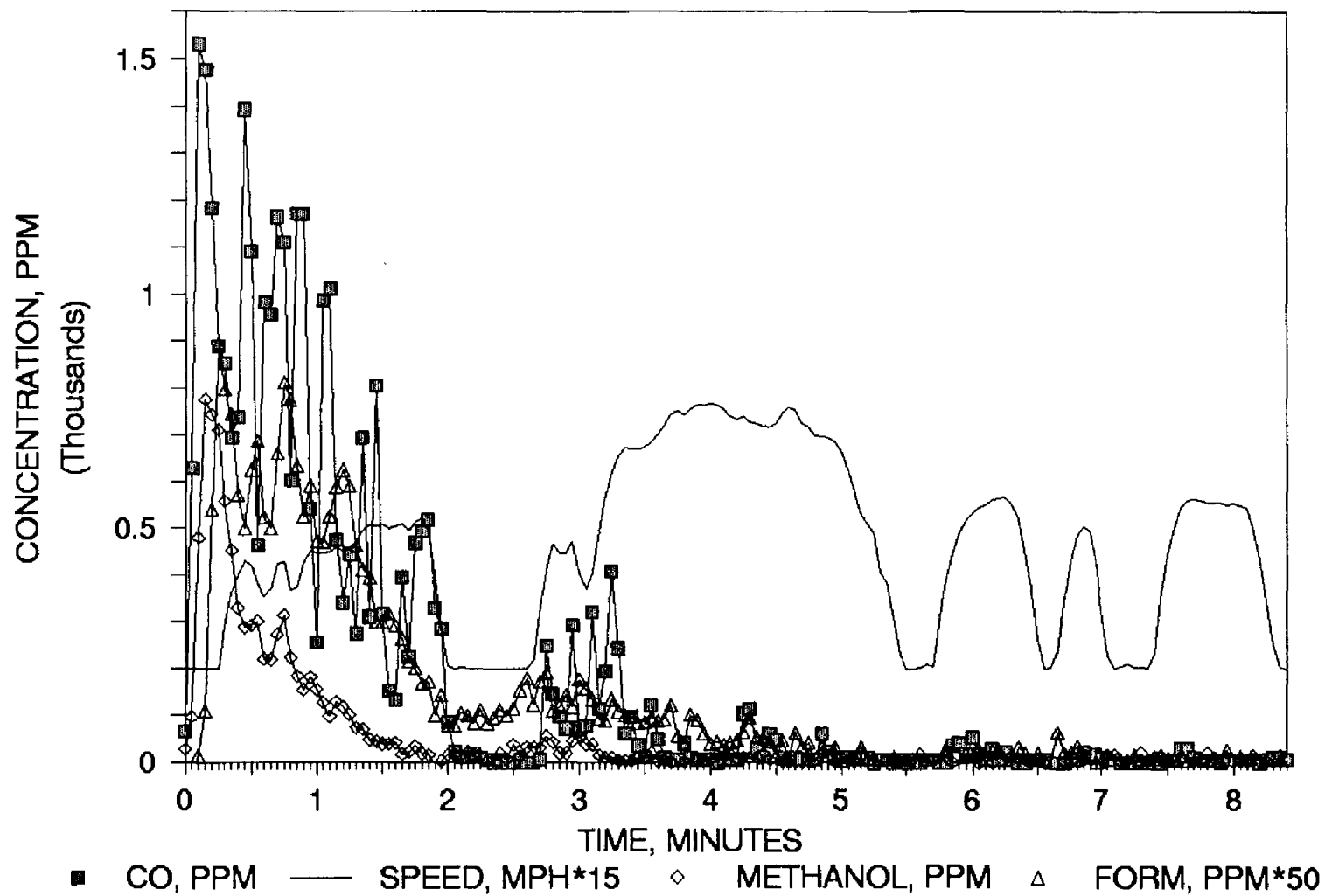


Figure 2. FTP Bag 1. 1988 Corsica. Speed vs.
Carbon dioxide, Methanol, and Formaldehyde

REMOTE SENSING MEASUREMENTS OF
CARBON MONOXIDE EMISSIONS
FROM ON-ROAD VEHICLES

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Failure of many urban areas to meet clean air standards for CO has increased pressure for stricter vehicle emission controls. To understand the impact of this strategy and/or to propose alternative, more effective control strategies, requires a better understanding of the emissions from vehicles during normal, on-road operation. This report describes instrumentation that is capable of remotely measuring the CO emissions from thousands of vehicles per day with a sensitivity of $\pm 1\%$ CO, which, for new vehicles, is approximately 10 grams per mile of CO. A prototype of this instrument was used in Denver, CO in January of 1989 during a study conducted in conjunction with researchers from the University of Denver, who have developed similar instrumentation. Emission measurements were made on approximately 4000 vehicles that were identified by make and model year from state vehicle registration records.

Introduction

Failure of many urban areas to meet clean air standards for CO has increased pressure for stricter vehicle emission controls. To understand the impact of this strategy and/or to propose alternative, more effective control strategies, requires a better understanding of the emissions from vehicles during normal, on-road operation. This report describes instrumentation that is capable of remotely measuring the CO emissions from thousands of vehicles per day with a sensitivity of $\pm 1\%$ CO, which, for new vehicles, is approximately 10 grams per mile of CO. A prototype of this instrument was used in Denver, CO in January of 1989 during a study conducted in conjunction with researchers from the University of Denver, who were contracted by GM to use similar instrumentation, which was developed there. Emission measurements were made on approximately 4000 vehicles that were identified by make and model year from state vehicle registration records.

Experimental

The systems operate by transmitting an infrared beam through the exhaust plume of each passing vehicle (see Figure 1). Three detectors monitor the infrared intensity in separate infrared spectral regions. The detector signals were measured immediately before and after a vehicle entered the infrared beam. Transmittance values for each detector channel were obtained by determining the ratio of post-car to pre-car signals. Concentrations of CO and CO₂ were derived from transmittances using polynomial equations which were best fits to calibration measurements of transmittance as a function of known concentrations. The most notable difference between the DU and GM instruments¹ is the use of a spinning gas filter correlation cell in the DU instrument¹. This cell enables the use of one detector to alternately measure the CO and reference signals, whereas the GM system uses separate detectors and measures all signals simultaneously. The DU system uses 16.6 millisecond time resolution for the CO and reference measurements and 8.3 milliseconds for the CO₂ measurement; the GM time resolution is 8.3 milliseconds for all channels². Signal to noise ratios for the DU system is approximately 1000 to one² versus 250 to one for the GM system.

The instruments were used to measure emissions from vehicles exiting I-25 onto southbound Speer Blvd., a major Denver traffic artery. This uphill ramp assured that most vehicles were modestly accelerating during measurement. The nearest on-ramp to this freeway was approximately two miles away, which guaranteed that all vehicles would be at operating temperature when our measurements took place. A video system recorded license plate numbers of all vehicles measured. Registration information provided age and make information for each vehicle.

The CO and CO₂ within an exhaust plume from a vehicle will disperse at an equal, but unknown rate. Although CO and CO₂ concentrations will vary rapidly with time, the CO/CO₂ ratio should be constant. Concentrations were therefore determined relative to a fixed pathlength (203 mm) and values of CO and CO₂ are reported as CO/CO₂ ratios.

Although the CO/CO₂ ratio measurements are good indicators of vehicle emission levels, the ratios can also be converted to percent CO levels, or also to gram-per-mile emission rates. Gram-per-mile (gpm) emission rates are a more conventional unit because it accounts for fuel economy.

Conversion from measured CO/CO_2 to gpm of CO requires knowledge of fuel density, the fraction of fuel weight present as carbon, and the fuel economy (miles per gallon) of the vehicle during the measurement. During the time of this study, Denver was participating in the oxygenated fuel program, whereby the fuel contained 2% oxygen by weight. Average fuel density was measured as 2745.6 grams/gallon and the average fraction of fuel weight present as carbon was 0.844. The most uncertain aspect of the conversion to gpm emission rates is the fuel economy of the vehicle. To minimize the uncertainties of this conversion, the measurements were carefully sorted by vehicle type, age and make and conversions were then based on fuel economy data for each subset of vehicles. The emission rates reported in this study, then, should be viewed as average, relative rates that could have substantial errors for any one vehicle.

The following equation was used to convert from CO/CO_2 ratios to gpm of CO emitted:

$$\text{CO(gpm)} = 2747.9 \text{ (g/gallon)} * 0.844 \text{ (g-C/g-fuel)} * Q / (1 + 1.175Q) * 28/12 \text{ (g-CO/g-C)} + X \text{ (mpg)}$$

In this equation, Q represents the measured CO/CO_2 ratio. Note that the emission rate is corrected for an assumed, but unmeasured, rate of hydrocarbon emission ($1.175 * Q$).

Results

Direct comparisons between the DU and GM measured CO/CO_2 ratios for 294 vehicles show good agreement. The correlation (r) between the two measurements is 0.84 and a least squares fit of GM versus DU data yields a slope of 0.88 ± 0.04 . Likely contributors of scatter in this plot are the low signal to noise ratios of the GM instrument and the susceptibility of the DU system to errors induced by the reference correction technique when particulate matter is present during measurements.

Three potential problems that might affect the accuracy of the remote measurements of CO/CO_2 ratios are: 1) Interference due to mixing of exhaust plumes from different vehicles 2) Infrared emission from hot exhaust 3) The technique by which transmittance measurements are corrected for scattering by particulate matter.

The GM and DU measurements each have the potential for inaccurately measuring an exhaust plume when remnants of a previous plume of different concentration remains. In the DU instrument, a software routine converts CO/CO_2 ratios to percent CO and CO_2 and plots each measured concentration of CO vs CO_2 . Measurements are discarded if the standard deviation of the linear fit to the slope exceeds 20%. Such a test is meant to detect changing CO/CO_2 ratios that would occur due to mixing of two plumes of different concentration ratios.

If a residual plume effect occurs, the effect would be expected to be most pronounced when measurements are made with short time separations between vehicles that emit very different concentrations of CO.

Data from this study show that vehicles which pass the instrumentation within one second of a high emitting (>5% CO) car, are less likely to be measured as low emitting (<1% CO) than cars which are 4 or more seconds behind high emitting cars. Also, cars within one second of a

high emitting car are more likely to have nonconstant CO/CO₂ ratios than are cars which are 4 or more seconds behind a high emitting car. The magnitude of these shifts in the frequency distribution of measurements is time dependent, i.e. the frequency (f) of measuring a clean car immediately after a dirty car follows the following relationship: $f(1 \text{ sec}) < f(2 \text{ sec}) < f(3 \text{ sec}) < f(4 \text{ sec}) \sim f(10 \text{ sec})$. Also the frequency of measuring nonconstant CO/CO₂ ratios follows the relationship: $f(1 \text{ sec}) > f(2 \text{ sec}) > f(3 \text{ sec}) > f(4 \text{ sec}) \sim f(10 \text{ sec})$. Nonconstant CO/CO₂ ratios are the consequence of the mixing of two plumes of differing concentrations.

This data suggests that a residual plume effect does occur and that the effect seems to last, on average, at least one second and possibly as long as 4 seconds. The DU nonlinearity test identifies plume nonlinearity, at least for many instances where a 0-1% CO vehicle follows closely behind a >5% CO vehicle. However, rejection of these measurements results in a sampling bias; a clean car (low CO) might not be measured if it follows closely behind a dirty car. The effect of this sampling bias is that the median CO measured in an exhaust plume is higher when a residual plume of >5% CO is present. It is impossible to determine from this data whether this increase in median CO is due only to sampling bias or is partially due to measurement error induced by the presence of a high level of CO.

The GM system was occasionally operated with no infrared source to determine if infrared emission from hot exhaust was detectable. Emission signals were detected in 17 of 220 measurements taken in this manner. The effect of infrared emission from hot gases or particulate would be to induce inaccuracies in the measurement of CO and CO₂ by both systems. Of the 17 vehicles that generated detectable infrared emission, 16 were either vans, pickup trucks. The factor most common to these vehicles seems to be the orientation of the tail pipe. Vans and pickup trucks frequently have tail pipes that direct hot exhaust perpendicular to the direction of travel, i.e., toward the instruments used for this study. This interference can be minimized by modifications to the instrumentation.

Alternately measuring CO and reference signals, as is done in the DU system, can potentially be a problem. In effect, each CO data point and every other CO₂ data point is being corrected by a reference data point being measured 8.3 milliseconds later. The turbulence behind most vehicles causes significant plume concentration fluctuations on this time scale. Simultaneous measurements of CO, CO₂ and reference signals will provide more accurate measures of CO and CO₂ concentrations in cases where particulate is present.

During this study, CO emissions from 3243 passenger cars and 887 light-duty trucks were measured. Figure 2 shows the fraction of the 3243 car measurements that are associated with each model year and also the fraction of all passenger car CO emitted by vehicles of each model year. It is clear that older vehicles emit a large fraction of the total CO. For example, 8.9% of the total number of passenger cars measured in this study were pre-1975 models (with a mean model year of 1970), yet they contributed 28.0% of all CO emitted by cars. Alternatively, 1987 through 1989 models contributed only 4.1% of CO from cars, but represented 23% of all cars measured.

An examination of the highest emitting passenger cars indicates that 50% of CO from cars is emitted by 8.1% of the cars. These cars, on average, were 12.3 years old and emit 90.4 gpm of CO. If all passenger

cars emitted at the rate measured for 1989 cars, emission rates would be reduced by 86.5%.

Discussion

The remote sensing technique described here can provide accurate measurements of CO/CO_2 , with only minor interferences that can be eliminated with instrument modifications. These ratios are, in themselves, useful indications of relative CO emission rates. The ratios can be converted to values of %CO with reasonable accuracy ($\pm 1\%$ CO). Conversions of the ratios to emission rates (gpm) requires knowledge of hydrocarbon emission rates and instantaneous fuel economy. Using careful estimates of these values probably provides reasonably accurate fleet average emission rates when large numbers of vehicle measurements are available.

This study was also affected by factors that cannot be assessed; for example, the effect of site selection, the Denver oxygenated-fuel program, altitude, and the effect of ambient temperature. These measurements are also not representative of other cities due to differences in vehicle fleets.

Conclusions

The data acquired during this study has provided important insight into fleet average CO emission rates at a site located in Denver, CO. To the extent that this site is typical of other urban areas within the United States, the results of this study can be useful in identifying cost-effective strategies for reducing urban CO pollution.

We have found that the majority of CO is emitted by a small minority of all vehicles. By examining the highest emitting vehicles, we find that 50% of the CO is emitted by 8.9% of all vehicles. By examining the oldest vehicles, we find that 57% of the CO is emitted by pre-1980 vehicles. In contrast, 1988 and 1989 vehicles contributed a combined total of only 2% of all CO emitted.

For CO control strategies, this data suggests that ambient CO levels can be impacted most by reducing emissions from the highest emitting vehicles rather than further reductions in emissions from new vehicles.

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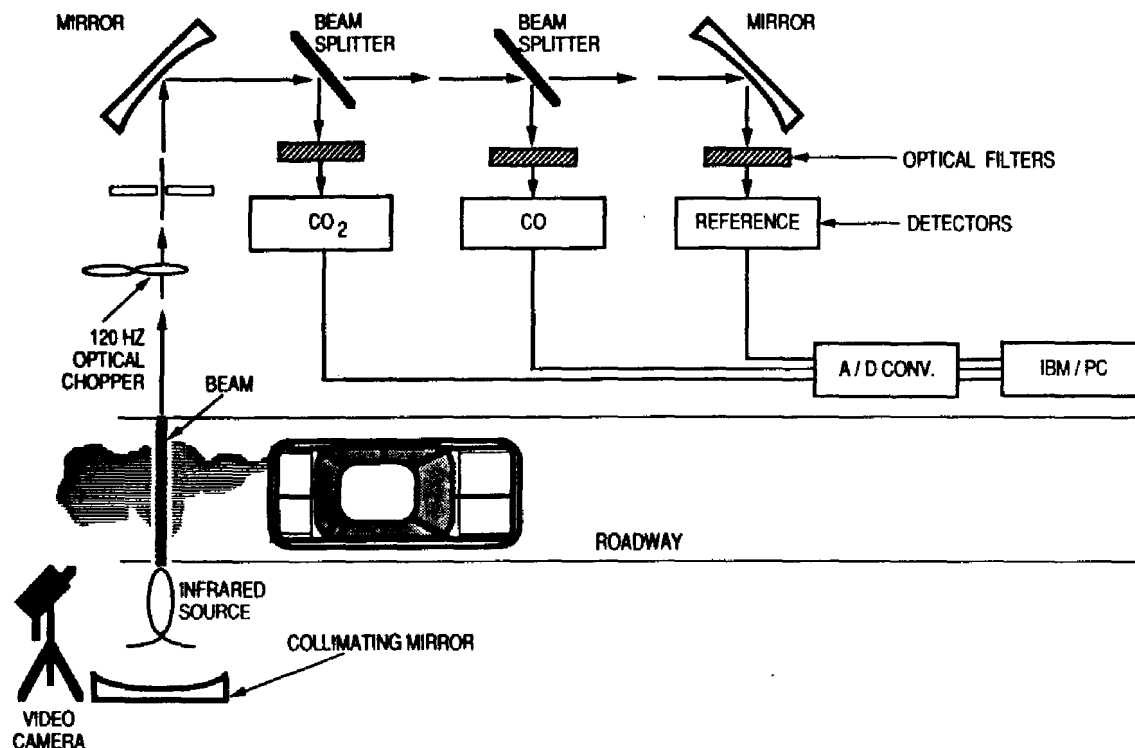


Figure 1. Schematic diagram of the GMR instrument for measuring CO/CO₂ ratios.

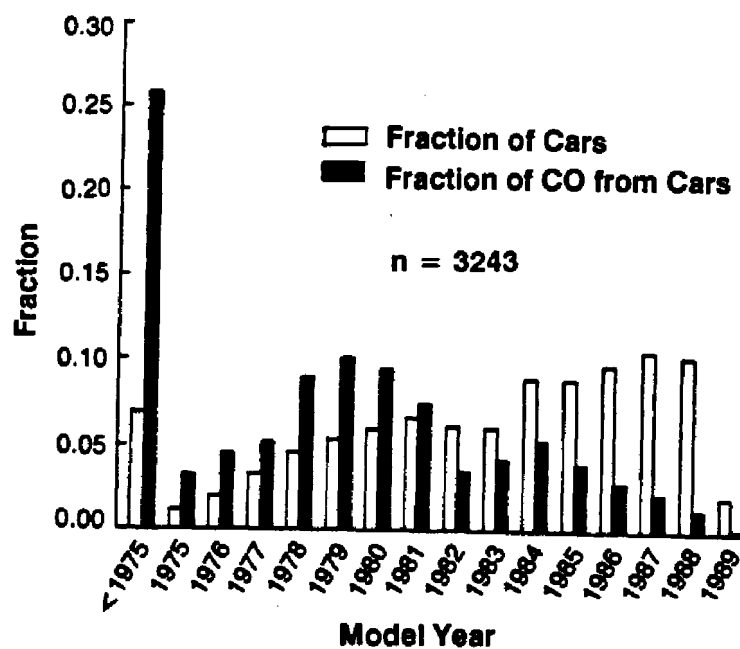


Figure 2. Distributions of CO emission rates and vehicle fraction by model year.

The Effect of Oxygenated Fuels
on Automobile Emission Reactivity

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Hydrocarbon emissions of vehicles are currently regulated on the basis of the total mass emitted without regard to the individual hydrocarbon's reactivity toward ozone formation. In this study individual hydrocarbons from tailpipe and evaporative emissions are weighted, relative to ethane, and summed according to their potential for ozone formation to determine the effect of temperature and fuel composition of the relative reactivity of the vehicle emissions. Two base fuels and two oxygenated fuels were studied at three temperatures (40, 75, and 90°F) following vehicle certification procedures as described in the Federal Register. The oxygenated fuels contained either ethanol or methyl tert-butyl ether (MTBE), blended to an oxygen content of 3% by weight. Both the evaporative emissions and the reactivity of these emissions were significantly greater for the oxygenated fuels than for the base fuels. Ethanol increased the total tailpipe emissions and the reactivity of those emissions compared to the summer base fuel. Lower reactivity of the tailpipe emissions when the MTBE blend was used resulted from lower total mass emissions including lower aromatic content. A non-oxygenated fuel was prepared from a low aromatic blend stock, used to produce the MTBE blend, by adding toluene to give the same octane rating as the MTBE blend for a comparison base fuel. The use of toluene, a low relative reactivity aromatic instead of the higher relative reactivity aromatics, produced a fuel that when used had a lower relative reactivity emissions than the summer grade fuel. The olefinic fractions were the major contributor to the reactivity of the emissions for all test conditions, regardless of the fuel used accounting for as much as 75% of the tailpipe and evaporative emissions reactivity.

Introduction

A primary reason for controlling automobile emissions is their role as precursors to ozone formation. Historically, the emissions have been regulated on the total hydrocarbon mass emitted. This approach fails to take into account the atmospheric reactivity differences of the individual hydrocarbons. Some compounds, such as 2-methyl-2-butene, have low emission rates, yet are highly reactive for ozone formation. Other compounds such as n-butane have high emission rates, but are relatively non-reactive. If in compliance with requirements for reduced total hydrocarbon mass emissions, compounds of relatively high reactivity remain, the ozone benefit will not be commensurate with the mass emission reductions.

Since the introduction of emission controls, tailpipe emissions of carbon monoxide and hydrocarbons have been reduced by over 90% (1). Significant tailpipe hydrocarbon (HC) and carbon monoxide (CO) reductions occurred with the introduction of oxidation catalytic convertors and oxides of nitrogen (NOx) reductions with the introduction of exhaust gas recirculating valves (EGR) and later 3-way catalytic converters. Today's 3-way catalyst tailpipe control systems also include exhaust oxygen sensors for computer control of the Air/Fuel Ratio. By maintaining the Air/Fuel Ratio at stoichiometric levels, emissions HC, CO, and NOx can be controlled for maximum reduction.

Reductions in total evaporative emissions can be realized by the reduction of the fuel vapor pressure (RVP) of the fuel which is largely determined by the amount of C4 and C5 paraffins present. Because these paraffins have relatively low reactivities, they may not contribute significantly to the overall reactivity of the emissions. Therefore, simply reducing the RVP of the fuel by reducing the C4 and C5 paraffins may not reduce the rate of ozone formation, commensurate with reductions of hydrocarbon mass emissions.

The addition of oxygenates such as methyl tert-butyl ether (MTBE) to gasoline is being used to reduce carbon monoxide emissions and to elevate fuel octane. Previous studies have examined the effect of oxygenated blends on hydrocarbon mass emission rates (2). The purpose of this paper is to examine the impact of oxygenated fuel additions on the ozone potential of motor vehicle emissions.

The reactivity scheme used in this study is based on the reaction rate of the organics with OH radicals. Reaction rate constants and relative reactivity data for each compound were obtained from the California Air Resources Board (3). Each compound was assigned a reactivity value relative to ethane which is assigned a relative reactivity of 1.0. A selected list of compounds and their reactivity values on both a volume and a weight basis are given in table 1.

Experimental

A 1988 Chevrolet Corsica was used for all tests. The car was equipped with current technology emission control equipment which includes a catalyst, an EGR valve, an Exhaust Oxygen Sensor (EOS) and computer control of the Air/Fuel ratio (A/F). The vehicle was powered by a 2.0L 4 cylinder engine with a throttle-body fuel injection system. No modifications were made to the engine, drive-train, or computer parameters. However, the fuel tank was modified by the insertion of a thermocouple plug to measure the fuel temperature during evaporative testing and a drain line to simplify the removal of waste fuel. The car arrived with 17 thousand miles and was driven 781.2 miles during the testing. All testing was done in accordance with the

rules and regulations as described in the Federal Register (4). A more comprehensive description of the test procedures and analytical techniques was reported by Stump, et al (5).

All evaporative and exhaust samples were analyzed for speciated hydrocarbons, oxygenates, and aldehydes by the methods reported by Stump, et al (6). The data was first reduced to the standard reporting format of grams/mile for exhaust data, of grams/test for diurnal and hot soak samples, and a grams/mile equivalent for evaporative emissions. The evaporative equivalent value was calculated

$$\text{Evap} = \frac{\text{Diurnal} + 3.01(\text{trips/day}) \times \text{Hot Soak}}{31.1 \text{ miles/day}}$$

Evap-Evaporative Equivalent (grams/mile)

Diurnal-Diurnal Emissions (grams/day)

Hot Soak-Hot Soak Emissions (grams/trip)

from the diurnal and hot soak results for each compound found in the evaporative samples. Each reported compound in the evaporative and tailpipe samples was multiplied by the associated relative reactivity index (ethane=1, toluene=7.3) and summed to produce an emission reactivity index (ERI). Tailpipe and evaporative ERI results are in the units of relative reactivity *

grams/mile. Class reactivity fraction and class mass fractions were also

$$\text{Emission Reactivity Index (ERI)} = \sum_{\text{all HC's}} \text{HC, g/mile} \times \text{Relative Reactivity}$$

calculated for all evaporative and tailpipe emissions. The data were then sorted by class and Carbon number from which the tables were prepared.

Calculations for the fuels were based on volume percentages and consequently the relative reactivities used were on a volume basis.

$$\text{Class Reactivity Fraction} = \frac{\sum_{\text{class}} \text{HC, g/mile}_{\text{class}} \times \text{Relative Reactivity}}{\sum_{\text{all HC's}} \text{HC, g/mile} \times \text{Relative Reactivity}} \times 100$$

$$\text{Mass Fraction} = \frac{\sum_{\text{class}} \text{HC, g/mile}_{\text{class}}}{\sum_{\text{all HC's}} \text{HC, g, mile}} \times 100$$

Four fuels were chosen for testing based on present use and

predictions of what fuels may be available if the use of oxygenated fuels becomes mandatory. The fuels were: a locally available unleaded summer grade

base fuel, a "splash blend" of 8.1% (v/v) ethanol fuel, a high

aromatic base fuel and a low aromatic reformulations with 16.5% (v/v) MTBE blend. Both of the oxygenated fuels contain 3% (wt) oxygen. Table 2 summarizes the characteristics of each fuel along with a listing of current national averages.

$$\text{Fuel Reactivity Index (FRI)} = \sum_{\text{all HC's}} \text{HC\%} \times \text{Relative Reactivity (by Volume)}$$

The regular unleaded summer grade gasoline was obtained from a local gasoline distributor and represents a regular unleaded gasoline distributed in North Carolina during the spring and early summer months. The fuel had an octane rating, (R+M)/2, of 87.6 and a RVP of 10.2 psi. The aromatic, olefin, and paraffin fractions of 46.7%, 11.5%, and 37.7% by volume respectively.

A portion of the summer grade fuel was splash blended with ethanol at

the 8.1% v/v to yield 3% oxygen by weight. In order to simulate possible actions of a local distributor, no attempt was made to reduce the RVP. As a result, a slight increase in the RVP (2.94%) and slight increase in the octane Rating (1.71%) was obtained. The resultant blend is believed to represent an ethanol blend that local distributors might produce.

Sun Oil Company was commissioned to prepare the MTBE blend used for this study. For this purpose, a low aromatic blend stock (LABS) was prepared and used for blending. MTBE was added at the 16.2% v/v level for a 3% by weight oxygen blend. The resultant fuel had a slightly higher RVP (0.95%) and octane (0.56%) than the unleaded summer grade base fuel. The 16.2% MTBE fuel contained 20.9% aromatic, 52.6% paraffin, and 10.3% olefins. An aromatic blend stock, consisting primarily of toluene, was added to the LABS to match the octane rating of the MTBE blend. This high aromatic fuel was tested as a base fuel for the MTBE blend.

Results and discussions

Relative reactivities based on volume, as opposed to the weight basis used for emissions data, were used to calculate the reactivity contribution for each compound in the fuel. Class and carbon number reactivities were summed and normalized for comparisons to the volume percentages (Table 3). A fuel reactivity index (FRI) for each fuel was calculated by weighting the volume fraction of each compound by the compound's volume reactivity and summing the results. The summer grade fuel had the highest FRI, 70.69. The 8.1% ethanol fuel prepared from the summer grade fuel had a FRI of 69.07, only slightly lower than the base fuel. The decrease in reactivity is attributed to the relatively low reactivity of ethanol.

The high aromatic fuel and the MTBE fuel were both prepared from a low aromatic blend stock which contained low concentrations of the reactive C9 aromatics. For both the high aromatic fuel and the MTBE fuel, the LABS was diluted with relatively low reactivity compounds, 16.2% MTBE and 26% toluene. The olefinic reactivity of the MTBE and the base fuel is similar to that of the summer base fuel, however the lower C9 aromatic content of the prepared fuels resulted in an overall FRI of 57.96 for the MTBE fuel and 48.86 for the high aromatic base fuel compared to the 70.69 for the summer grade fuel. The high Aromatic fuel was prepared by the addition of toluene to the LABS such that the octane rating matched the 89.6 octane rating of the MTBE fuel. Toluene accounted for 30.69% of the total volume compared to only 6.67% in the MTBE fuel. However, toluene has a low relative reactivity and did not contribute significantly to the overall FRI.

The olefin fractions of the fuels are only 8.5- 11.5% of the total fuel by volumes, but represent 59.4-66.5% of the FRI. The major portion of the olefin reactivity comes from the C5 olefins which have a very high relative reactivity value. The C5-C8 olefins as a whole are 4 times more reactive than any of the aromatics and almost 10 times more reactive than the xylenes which contribute roughly 8% of the total volume. This amount is almost the same volume percent as the total olefin fraction. The total aromatics, while contributing 20.9-37.7% of the volume, contribute 16.7-28.1% of the FRI. The paraffins which are the major portion of the fuel on a volume basis, but represent only 10.6-14.7% of the total FRI. The oxygenates have relative reactivity's similar to the paraffins and did not contribute significantly to the overall fuel reactivity.

As expected evaporative mass emission rates significantly increased at test temperatures of 90°F (Table 4). At 90°F the high aromatic fuel had lower mass emission rates than did the other fuels. At 40°F and 75°F the evaporative mass emission rates for all fuels were within 0.013 grams/mile

and indicated no significant trends between oxygenated and non-oxygenated fuels. At 90°F however, the summer base fuel had a three fold increase in evaporative mass emissions compared to the 75°F test, while the ethanol fuel had an evaporative mass emissions increase of almost tenfold. A similar tenfold increase occurred with the MTBE blend, but not with the non-oxygenated high aromatic base fuels. In all cases the increase in evaporative emissions resulted in higher ERI values for the evaporative emissions, due to the increased mass emission rates.

Since the evaporative emissions are predominately paraffins, the ERI increases are not directly proportional to the mass emission rate increases. Paraffins typically account for as much as 73% of the evaporative emission, with n-Butane contributing 23% to the total mass. At 90°F, n-butane accounted for 44.5% of the total evaporative mass, but on a reactivity scale, n-butane accounted for less than 20% of the evaporative ERI. The major contributor to the evaporative ERI are the olefins, which account for an average of 68.92% of the ERI at 90°F (Tables 5 and 6).

The evaporative mass and consequently ERI values of the 90°F tests were significantly higher for the oxygenated fuels than for either of the non-oxygenated fuels. Even though the oxygenates represented significant fractions of the 8.1% ethanol and 16.2% MTBE fuels they represented less than 1.2% of the total mass in the evaporative samples (Table 7). The absence of the oxygenates in the evaporative samples and the elevated mass emission rates indicate that the evaporative canister may be selectively retaining the oxygenates and displacing the hydrocarbons.

At all three temperatures the tailpipe emissions of the 8.1% ethanol fuel were found to have greater ERI rates than the summer grade exhaust due to the greater mass emission rates for the ethanol fuel (Table 8). At 75°F, the ethanol fuel had a higher total mass emission rate yet, because of the reduced aromatic emission rates, the resultant exhaust was less reactive. At 40°F and 90°F the tailpipe mass emissions and ERI values were greater for the ethanol fuel than for the summer grade fuel.

At all three temperatures the high aromatic fuel and the 16.2% MTBE fuel had lower total mass emission rates. The lower mass emission rates coupled with the inherently lower relative reactivity of the fuel components resulted in lower tailpipe ERI values. In all tests the aromatic ERI rates were reduced when these two fuels were used. This is a direct result of the lower C9 aromatic content of these fuels. Total aromatic concentrations in the emissions for the high aromatic fuel and the summer grade fuel were similar. The high aromatic emissions contained large percentages of toluene whereas the summer grade emissions contained large C9 aromatic fractions, reflecting the aromatic composition of the fuels. Since toluene has a low relative reactivity, it did not raise significantly the ERI rates of the tailpipe emissions for the high aromatic fuel.

The high aromatic fuel demonstrated most drastically the effect of the fuel composition on tailpipe ERI (Tables 11, 12, and 13). Mass emission rates for the high aromatic fuel were 9.42, 18.43, and 33.81% lower than those for the summer grade fuel for the respective test temperatures, 40, 75, and 90°F. Yet those emissions were 30.75, 23.21, and 42.67% less reactive than those of the summer grade fuel. The aromatic mass fraction of the high aromatic exhaust was of similar proportions to the summer grade fuel, but because the aromatic fraction is predominately toluene and not the C9 aromatics found in gasoline, the exhaust from the high aromatic fuel produced lower ERI values.

Similarly, the MTBE blend contained low aromatic concentrations, which

was reflected in the exhaust. When the MTBE fuels (20.92% aromatic) was used, the aromatic content of the total tailpipe mass emission ranged from 13.12% to 25.37%. The low total mass emission rates coupled with the reduced FRI resulted in lower tailpipe ERI rates for the MTBE fuel.

The MTBE fuel also contained low C9 aromatic concentrations, but did not contain large concentrations of toluene. Thus the aromatic mass emitted by the MTBE fuel was less than the other fuels. However the ERI decrease caused by the low aromatic emission rates were offset slightly by increased isobutylene formed during combustion of MTBE (Table 14). Isobutylene ERI values increased an average of 420% when the 16.2% MTBE fuel was used. Yet even with the isobutylene increases the 16.2% MTBE fuel resulted in the lowest olefinic ERI at test temperatures of 40°F and 75°F. The low olefinic fraction of the fuel and the lower mass emission rates combined to produce the lower olefinic ERI rates.

The average relative reactivity index (ARRI) was calculated for each sample (Table 9). Generally, the data showed that the high aromatic and 16.2% MTBE fuels produced lower ARRI values than the summer grade and ethanol fuels for reasons discussed previously. However the data also showed a marked decrease in the ARRI of the ethanol tailpipe emissions at 75°F. Total mass emissions and class distribution values were within expected ranges. However on a relative reactivity scale, the 75°F test with the ethanol fuel failed to give an increase in ERI commensurate with the mass emission rate increase as compared to the 75°F summer grade test. As a result the ARRI was drastically lower than was expected. For all tests the ARRI values failed to show any distinct trends between temperature or fuel.

$$\text{Average Relative Reactivity Index (ARRI)} = \frac{\sum_{\text{all HC's}} \text{HC, g/mile} \times \text{Relative Reactivity}}{\sum_{\text{all HC's}} \text{HC, g/mile}}$$

A closer examination of the class and carbon number distributions of the tailpipe emissions from the 75°F test with the ethanol fuel revealed that the C8 olefinic contribution to the ERI was less than with the other fuels and temperatures tested (Table 10). For all of the tests, the C8 olefin emissions account for less than 1% of the total mass. However when that mass is multiplied by the large relative reactivity value of the C8 olefins (194.9) their importance greatly increased. On the relative reactivity basis the C8 olefins accounted for as much as 6.2% of the total ERI. The inconsistency found in this data is possibly attributable to missing or incomplete data used in interpreting the chromatographic results. Chromatographically the C8 olefins appear to be minor peaks when compared to the relatively large surrounding peaks such as iso-octane or 2,5 dimethyl hexane which all elute within a five minute window. Within this five minute window there are ten compounds tentatively identified as C8 olefins half of which are normally observed in the samples. One might be tempted to dismiss the "minor" peaks as having very little importance to the overall analysis however, this study underscores the value of accurately identifying and quantifying even the minor compounds found in the samples.

Conclusions

Reducing the Reid Vapor Pressure by lowering the concentration of n-Butane may reduce the overall evaporative mass emissions, but may not lower the ozone potential of the hydrocarbon emissions commensurately.

Oxygenates increase the evaporative emission rates, possibly attributable to the evaporative canister selectively retaining the oxygenates.

The ERI rates increased with the use of ethanol due to the increased mass emission rates that occur with the use of ethanol.

Total tailpipe emission rates and ERI values decrease with the use of MTBE, in spite of the increased isobutylene emissions. The lower overall mass emission rates of the MTBE fuel combined with the lower aromatic and olefinic concentrations, of the fuel reduced the tailpipe reactivity index.

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Table 1. Selected Relative Reactivity Values

Compound	Reactivity (related to Ethane)	
	by Volume	by Weight
C8 Olefins	727.3	194.9
C5 Olefins	545.5	233.9
Isoprene	363.6	160.5
1,3-Butadiene	242.9	135.0
trans-2-Butene	231.6	124.2
Terpenes	206.5	45.6
cis-2-Butene	204.0	109.3
C9 Aromatics	109.1	24.4
Ethanol	10.3	6.9
Toluene	22.5	7.3
n-Butane	9.2	4.8
Benzene	4.7	1.8
Ethane	1.0	1.0
Methane	0.0	0.1

Table 2. Test Fuel Specifications

Fuel Property	National Summer Grade (1) Average	Range	Commercial Summer Grade	Summer Grade/ 8.1 % Ethanol	High Aromatic	16.2 % MTBE
Regular Unleaded						
Specific Gravity	0.7406	(0.718-0.7594)	0.7428	0.7465	0.7383	0.7146
RVP, psi (2)	10.0	(7.7-12.2)	10.2	10.5	10.1	10.6
Octane ((R+M)/2)	87.1	(84.4-90.7)	87.6	89.1	89.4	89.6
Distillation, Deg. F						
IBP (3)	92.0	(85-106)	89.6	84.0	96.8	96.8
10 %	119.0	(107-138)	118.4	114.0	131.0	123.8
50 %	205.0	(143-231)	212.0	196.0	199.4	177.8
90 %	341.0	(306-367)	356.0	360.0	269.9	284.0
End Point	420.0	(378-482)	413.6	420.0	399.2	395.6
Volume %						
Paraffins	58.1	(35.0-72.9)	48.62	44.68	45.58	52.61
Olefins	12.4	(0.8-37.0)	10.33	9.49	8.42	9.90
Aromatics	29.5	(15.8-41.5)	37.93	34.86	45.60	20.92
Benzene	1.6	(0.6-4.7)	1.39	1.28	0.45	0.53
Toluene	(4)	(4)	6.19	4.28	6.66	30.69
MTBE	<0.5	(0.0-5.7)	ND (3)	ND (3)	ND (3)	16.20
Ethanol	<0.9	(0.0-9.0)	ND (3)	8.10	ND (3)	ND (3)

(1) Source: MVMA (1987) (2) RVP-Reid Vapor Pressure (3) ND-Not Detected (4) Data unavailable
 (5) Oxygenates and Unknowns represent the remainder of the percentages in all tables

Table 3.

Fuel Compositions, by Class
Volume %, (FRI %)

	Paraffins	Olefins	Aromatics	Oxygenates and Unknowns	Fuel Reactivity Index
Summer Grade	46.7 (10.6)	11.5 (59.4)	37.7 (28.1)	4.1 (1.9)	70.69
8.1% Ethanol	57.9 (13.0)	11.5 (65.3)	26.6 (20.4)	9.0 (1.3)	69.07
High Aromatic	45.4 (13.2)	8.5 (59.6)	45.8 (26.9)	0.4 (0.2)	48.86
16.2% MTBE	52.6 (14.7)	9.9 (66.5)	20.9 (16.7)	16.6 (2.1)	57.96

Table 4.

Evaporative Emission Rates
grams/mile (Emission Reactivity Index)

Fuel	40°C	75°C	90°C
Summer Base	0.0159 (0.459)	0.0542 (1.169)	0.1562 (2.740)
8.1 % Ethanol	0.0261 (0.703)	0.0516 (1.142)	0.4918 (8.959)
High Aromatic	0.0190 (0.415)	0.0444 (1.112)	0.2450 (3.677)
16.2 % MTBE	0.0178 (0.512)	0.0417 (0.853)	0.3581 (6.636)

Table 5.

Class percentages of Evaporative Emissions
by Reactivity

	40°F			75°F			90°F		
	paraffins	olefins	aromatics	paraffins	olefins	aromatics	paraffins	olefins	aromatics
Summer Base	11.29	61.33	23.46	11.55	48.94	37.35	23.05	62.74	13.36
8.1 % Ethanol	13.84	57.59	24.81	16.53	48.47	33.08	23.13	73.70	2.92
High Aromatic	14.39	64.97	18.98	12.74	62.43	24.08	26.53	63.83	9.28
16.2% MTBE	11.23	40.01	47.18	18.02	65.81	15.75	21.90	75.39	2.53

Table 6.

Organic class Reactivity Distribution of Evaporative Emissions
Emission Reactivity Index

	40°F			75°F			90°F		
	paraffins	olefins	aromatics	paraffins	olefins	aromatics	paraffins	olefins	aromatics
Summer Base	0.5183	0.2815	0.1077	0.1350	0.5721	0.4367	0.6317	1.7193	0.6332
8.1% Ethanol	0.0974	0.4051	0.1745	0.1888	0.5536	0.3778	2.0725	6.6027	0.2615
High Aromatic	0.0598	0.2698	0.0788	0.1416	0.6941	0.2678	0.9755	2.3466	0.3415
16.2% MTBE	0.0574	0.2047	0.2426	0.1536	0.5611	0.1343	1.1020	5.0971	0.6032

Table 7.

Oxygenate Evaporative Concentrations

	8.1% Ethanol Fraction		
	DIURNAL(% TOTAL)	HOT SOAK (% TOTAL)	EVAP EQUIV (% TOTAL)
40	0.00696 (1.461)	0.00609 (1.011)	0.000817 (1.009)
75	0.00783 (0.510)	0.00624 (0.868)	0.000855 (0.714)
90	0.01044 (0.868)	0.01363 (0.720)	0.001653 (0.112)

	16.2% MTBE Fraction		
	DIURNAL(% TOTAL)	HOT SOAK (% TOTAL)	EVAP EQUIV (% TOTAL)
40	0.006573 (2.247)	0.00445 (1.035)	0.000648 (1.260)
75	0.007750 (0.567)	0.00290 (0.371)	0.000508 (0.421)
90	0.183667 (0.750)	0.01092 (0.476)	0.006712 (0.067)

Table 8.

Tailpipe Emission Rates
grams/mile (Emission Reactivity Index)

Fuel	40°C	75°C	90°C
Summer Base	0.5552 (14.387)	0.3597 (10.677)	0.3195 (7.474)
8.1% Ethanol	0.7880 (18.566)	0.5674 (8.668)	0.5316 (13.667)
High Aromatic	0.5029 (10.035)	0.2934 (8.199)	0.2114 (4.285)
16.2% MTBE	0.3386 (8.818)	0.2554 (6.421)	0.3041 (6.862)

Table 9.

Average Relative Reactivity Index (ARRI)

	Evaporative		Exhaust	
	40°F	75°F	40°F	75°F
Summer Base	28.87	21.57	25.91	29.68
8.1% Ethanol	26.93	22.13	23.56	15.28
High Aromatic	21.84	25.02	19.95	27.94
16.2% MTBE	26.04	25.14	28.76	20.46

Table 10.

C8 Olefin Reactivity Emission Rates
% of ERI (% of Total Mass)

	40°F	75°F	90°F
Summer Base	5.057 (0.679)	4.503 (0.708)	0.783 (0.085)
8.1% Ethanol	4.042 (0.487)	1.004 (0.108)	4.706 (0.622)
High Aromatic	3.172 (0.324)	2.853 (0.266)	6.217 (0.635)
16.2% MTBE	4.973 (0.649)	5.463 (0.693)	1.846 (0.195)

Table 11.

Class percentages of Tailpipe Emissions
% of Emission Reactivity Index

	40°F		75°F		90°F	
	paraffins	olefins	aromatics:	paraffins	olefins	aromatics:
Summer Base	10.66	58.89	29.72	9.936	49.65	38.87
8.1 % Ethanol	10.34	54.96	32.01	8.907	56.51	31.91
High Aromatic	11.12	68.16	20.19	14.67	56.04	27.43
16.2% MTBE	11.63	59.49	23.48	9.576	60.34	28.84

Table 12.

Class Reactivity Distribution of Tailpipe Emissions
Emission Reactivity Index

	40°F		75°F		90°F	
	paraffins	olefins	aromatics:	paraffins	olefins	aromatics:
Summer Base	1.5337	8.4725	4.2758	1.0609	5.3011	4.1501
8.1% Ethanol	1.9197	10.2039	5.9430	0.7721	4.8983	2.7660
High Aromatic	1.1159	6.8399	2.0261	1.1861	4.5947	2.2490
16.2% MTBE	1.0255	4.8663	2.0250	0.6149	3.8742	1.8518

Table 13.

Mass Distribution of Tailpipe Emissions
by Organic Class

	40°F		75°F		90°F	
	paraffins	olefins	aromatics:	paraffins	olefins	aromatics:
Summer Base	46.76	19.98	33.25	47.70	17.99	34.31
8.1% Ethanol	46.65	17.64	35.72	45.87	19.81	34.32
High Aromatic	45.78	19.92	34.75	42.27	19.42	38.3
16.2% MTBE	52.89	22.69	24.42	53.17	21.45	25.37

Table 14.

Isobutylene Reactivity Emission Rates
Emission Reactivity Index (% ERI)

	40°F	75°F	90°F
Summer Base	0.348 (2.42)	0.206 (1.93)	0.231 (3.09)
8.1% Ethanol	0.380 (2.05)	2.820 (3.32)	0.427 (3.12)
High Aromatic	0.491 (4.89)	0.231 (2.82)	0.277 (6.47)
16.2% MTBE	1.266 (14.35)	0.875 (13.62)	1.085 (15.82)

FTIR: FUNDAMENTALS AND APPLICATIONS IN THE ANALYSIS OF DILUTE VEHICLE EXHAUST

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Fourier transform infrared (FTIR) spectroscopy has been shown to be a valuable tool in the analysis of complex gaseous mixtures, such as dilute vehicle exhaust. Regulated and non-regulated vehicle emissions have been routinely sampled and analyzed using prototype instrumentation developed in this laboratory, and in several other laboratories over the last decade. More recently, commercial versions of these FTIR analyzers have become available through several manufacturers. This paper reviews data acquisition and processing techniques employed by several of the prototype and commercial FTIR systems. Techniques utilized by the FTIR emissions analyzer developed in this laboratory, and several of its unique capabilities, are also addressed in detail. In addition, experiments designed to investigate the effects of instrumental and environmental parameters that alter spectral line widths, and consequently affect the accuracy of this high resolution system, are described. The results of these studies indicate that routine variations in parameters, such as instrument resolution, sample temperature and pressure have minimal effects on the accuracy of the analysis of low concentrations of nitric oxide.

Introduction

Fourier transform infrared (FTIR) spectroscopy has been shown to be a valuable tool in the analysis of complex gaseous mixtures, such as dilute vehicle exhaust. Regulated and non-regulated vehicle emissions have been routinely sampled and analyzed using prototype instrumentation developed in this laboratory,^{1,2,3,4} and in several other laboratories over the last decade.^{5,6,7,8,9} There are several reasons which explain the increase in the popularity of FTIR spectroscopy as a technique for the analysis of vehicle emissions. Unlike conventional emissions analyzers, the FTIR is a single instrument capable of performing simultaneous multicomponent analyses. In addition, FTIR systems have been shown to be more practical, and as sensitive as, wet chemical techniques for the analysis of non-regulated emissions such as methanol and formaldehyde.⁴ In more recent years, commercial versions of these FTIR analyzers have become available through several manufacturers. This paper reviews data acquisition and processing techniques employed by several of the prototype and commercial FTIR systems. Techniques utilized by the FTIR emissions analyzer developed in this laboratory, and several of its unique capabilities, are also addressed in detail. In addition, instrumental and environmental parameters that alter spectral line widths, and consequently affect the accuracy of this high resolution system, are explored.

The FTIR analyzers currently in use employ a variety of data acquisition and processing techniques to quantify gaseous species. Most often, the frequencies of unique absorption bands are used to identify the chemical species, and peak heights or peak areas are used to determine their concentrations. Linear processing techniques, such as masking,¹⁰ subtraction,^{7,9} and linear regression programs^{5,6,8} are used if the behavior of such absorption bands obeys Beer's Law. If the behavior of these bands deviates from Beer's Law, nonlinear techniques such as least squares fitting programs, which rely on higher order regressions, must be employed.^{8,11}

Selecting "interference free" absorption lines for the quantification of gaseous species in complex mixtures is often a difficult task. If the resolution of the spectrometer is not sufficient, interferences can arise from overlapping lines. Often times, it is difficult to correct for such interferences. It is for this reason that high resolution FTIR spectroscopy is preferred for quantification. Least squares fitting programs have been used in conjunction with lower resolution spectroscopy with reasonable success.¹¹ There are several advantages and disadvantages associated with high resolution spectroscopy. Typically, high resolution spectra require greater data acquisition times, are noisier than the lower resolution counterparts, and require the use of computers with greater memory and processing capabilities. Higher quality (higher cost) interferometers are needed to acquire precise, high resolution infrared spectra. In addition, to maximize resolution infrared beam diameters must be kept to a minimum, thus affecting instrumental throughput and sensitivity.

The advantages of high resolution systems are illustrated using an infrared spectrum of dilute vehicle exhaust (Figure 1). It is evident that absorption lines associated with water and carbon dioxide dominate the spectrum. Without the ability to resolve the unsaturated lines from the saturated lines, only a few, rather narrow spectral regions remain free from interferences. The physical or chemical removal of water or carbon dioxide from such samples improves the utility of the spectral region, but presents several problems. Techniques used to eliminate water will also remove water

soluble components, such as methanol and formaldehyde. In addition, it is difficult to perform quantitative analyses after "drying" a sample unless the amount of water and water solubles removed can be accurately determined. An alternate technique used to remove water and carbon dioxide absorption bands is spectral subtraction. Most often, in the case of raw or diluted exhaust samples, the water and carbon dioxide absorption lines are saturated and cannot be completely eliminated by linear subtraction methods. If used properly, high resolution systems can take advantage of the unsaturated regions of the spectrum and perform interference free analyses of several regulated and non-regulated emissions components (Table I).

In addition to the identification and quantification of exhaust components, several of the commercially available systems provide time-resolved emission data. Coupled with direct sampling devices, such as a dilution tube^{3,4} or Constant Volume Diluter (CVD),¹² these systems are useful for evaluating factors that affect emission levels during transient phases of vehicle tests. Relationships between variables such as road speed or post catalyst temperatures and emission levels of several components can be established. Examples of some of the information available using time-resolved data acquired on the FTIR emissions analyzer developed in this laboratory are presented in Figures 2 and 3.

Restricted by computer processing and storage capabilities, some FTIR analyzers are limited to acquiring integrated or signal averaged data, as opposed to real-time data. Consequently, such systems are often coupled with indirect sampling devices, such as Tedlar bags or other sample containers.^{7,9} These systems have also been used with direct sampling devices to analyze emissions during steady state vehicle experiments, or to obtain integrated emission values for transient cycles.⁹

Experimental Methods

Instrumentation

The FTIR emissions analyzer developed in this laboratory is comprised of three basic subsystems; 1) the infrared spectrometer and optical accessories for gas phase measurements, 2) the data acquisition and processing system, and 3) the associated sampling hardware. The high resolution Fourier transform infrared spectrometer (Nova-Cygni 120 model, Mattson Instruments, Inc., Madison, WI) is a research grade instrument capable of acquiring quality, eighth wavenumber (0.125 cm^{-1}) spectra. (Due to computer limitations and time resolution constraints, the system is operated at a resolution of 0.25 cm^{-1} , and the interferograms are zero filled to an effective resolution of 0.125 cm^{-1}). The spectrometer is equipped with a water cooled, glow bar source and a narrow band MCT detector with a linearized preamplifier. A variable pathlength, multi-pass gas cell (Wilks 20 Meter - Model 9020) with potassium bromide windows, is used exclusively at the 14th order setting (21.75 meters) to improve the sensitivity of the system for all chemical species.

Data acquisition and processing is controlled by a Concurrent computer equipped with an array processor (Model 5450). The computer is a multi-user system based on the UNIX operating language. The data acquisition and processing routines were developed at the Ford Motor Company Scientific Research Laboratories. This software was designed for the specific purpose of (but not limited to) analyzing multicomponent gas phase samples composed

of chemical species typically found in dilute vehicle exhaust. The system can be used to acquire either time-resolved or signal averaged data. It is capable of co-adding, transforming, and analyzing high resolution spectra in 3 second intervals. Currently, 24 distinct components are monitored on a real-time basis. The real-time detection limits for these components are reported in Table II. It should be noted that the detection limits for the concentration ranges most often encountered during vehicle testing are listed. Other ranges, which are more appropriate for atmospheric concentration levels, provide greater sensitivity for a limited number of species. Signal averaging can be employed during steady-state engine or vehicle experiments to improve detection limits. The hardware and software used with the system are capable of monitoring up to 50 individual components. Species other than those listed in Table II can be added to the system by acquiring a representative reference spectrum, developing an effective mask, and incorporating the calibration factor into the existing software. This operation is performed routinely in our laboratory.

The sampling hardware consists of high flow rotary vane and direct drive high vacuum pumps, an absolute pressure meter, and 0.5 in. OD stainless steel transfer lines and valves. Direct sampling of dilute exhaust is performed using the high flow pump (Model 5KC48PG656BS, General Electric, Fort Wayne, IN). The high vacuum pump (Model E2M-18, Edwards, Sussex, England) accommodates samples acquired indirectly, such as those contained in Tedlar bags or other sample vessels. Either the high flow or the high vacuum pump can be used to sample pressurized gas cylinders directly. The reference spectra used for quantitative analyses were acquired at sample pressures of approximately 933 mbar (700 torr). To prevent inaccuracies due to line broadening, the absolute pressure meter (Balzers - Model APG 010) is used to monitor sample pressures, so that they can be maintained at or as close to 933 mbar as possible.

Instrumental and Environmental Parameters and Their Effects on the Accuracy of this System

As mentioned above, the quantitative capabilities of the FTIR emissions analyzer developed in this laboratory are based on high resolution infrared spectroscopy. A procedure called "masking"¹⁰ is used to both identify and quantify absorptions in the sample spectra. A mask consists of select groups of spectral channels called segments. The segments are chosen from the unsaturated regions of the spectrum. Several channels are used to form either the background or signal segments of the mask. Background segments are used to determine the baseline of the sample spectrum in a given region. Ideally, background segments contain data channels to the immediate right and left of the signal channels. Signal segments are used in combination with the background segments to determine the area under an absorption band. Instrumental and environmental factors that alter spectral line widths can affect the accuracy of the high resolution masking technique. The general effect of variations in spectral line widths on the accuracy of the masking technique is illustrated in Figure 4. The extent of these effects vary depending on the nature of the absorbing species and the mask used. For example, masks for chemical species which have very narrow absorption bands, such as CO₂ and NO, may contain as few as one or two channels in their signal segments. If the instrumental resolution is insufficient, or if natural line widths are broadened due to an increase in sample pressure or temperature, the spectral line widths of such species will increase. In such cases, the channels chosen for the background segments may be skewed or shifted upward due to the line broadening, while the signal channels are simultaneously

shifted downward. Consequently, the areas determined by the mask segments will be less than those areas established using the reference spectra. In such cases, the accuracy of the masking technique is affected.

Several experiments were designed to investigate the effects of variations in spectral line widths on the accuracy the system. The experiments were performed using static gas phase samples from a high pressure cylinder containing a low concentration nitric oxide diluted with nitrogen. The natural line widths of nitric oxide absorptions are less than the resolution of the analyzer, therefore, the effects of variations in spectral line widths are expected to be greatest for this species. The cylinder (19.8 ppm \pm 1% NO) was obtained from AIRCO (Murray Hill, NJ), and its content was certified by the Ford Motor Company Gas Standards Laboratory. All studies were performed using the prototype hardware and the software developed at Ford Motor Company.

Results

Temperature Study

The temperature study encompassed temperature fluctuations that might be seen under normal atmospheric variations and under more extreme variations. (The use of heated raw exhaust samples versus room temperature dilute exhaust samples has been a issue of recent debate). A heating jacket (Foxboro Company - Model 500-0109) designed specifically for the Wilks gas cell, was used to control the sample temperature. Thermocouples were placed between the blanket and the cell, and inside the outlet port of the cell to monitor the temperatures of the exterior of the gas cell and of the sample gas. Temperature differences as great as $\sim 35^{\circ}\text{F}$ between the exterior of the cell and the sample gas were seen at higher sample temperatures ($\sim 160^{\circ}\text{F}$). Although the gas cell is rated for temperatures as high as 230°F , the sample temperatures were maintained below $\sim 150^{\circ}\text{F}$ to safely accommodate these temperature differences. Spectra were acquired at four temperatures, ranging from room temperature to $\sim 140^{\circ}\text{F}$.

If the gas obeys the ideal gas law, a inverse linear relationship between sample temperature and instrument response is expected. (If the pressure and the volume of the cell remain the same, an increase in temperature will result in a decrease in the number of molecules in the lightpath). The theoretical relationship between instrument response (R) and sample temperature (T) developed using the ideal gas law and the instrument response at 84°F is the following:

$$R = (-0.034 \text{ ppm}/^{\circ}\text{F})T + 23.1 \text{ ppm.}$$

The plot of instrument response as a function of sample temperature is presented in Figure 5. A linear regression of these data was performed and it was determined that the experimental relationship between instrument response and sample temperature is equivalent to the theoretical relationship (within experimental error) for the given concentration of nitric oxide. (slope = $-0.037 \text{ ppm}/^{\circ}\text{F}$, intercept = 23.4 ppm , and a correlation coefficient = 0.996). In addition, the linear subtraction of a spectrum acquired at room temperature from one acquired at 140°F indicates no appreciable line broadening with increasing temperature.

Pressure Study

The direct sampling devices routinely used with the FTIR emissions analyzer developed in this laboratory are open to the atmosphere. Thus, significant ambient pressure changes during a vehicle or engine test, such as passing storm fronts, will cause sample pressure changes which may impact the system's accuracy. In addition, there is some concern that results obtained using the commercial version of this instrumentation in testing facilities that are located at higher altitudes (with ambient pressures below the recommended sampling pressure of 700 torr) such as Denver, Colorado, will not be comparable to results obtained at other testing facilities. To address these issues, a pressure study was undertaken to establish the effects of ambient pressure changes on the accuracy of system. The analyzer's performance was characterized for nitric oxide at pressures ranging from approximately 933 mbar to 150 mbar.

If the ideal gas law is applied to the case of the pressure study, a direct linear relationship between sample pressure and raw instrument response is expected. If the raw instrument response was corrected using the ratio of the reference pressure (933 mbar) to the sample pressure, the system should provide accurate analyses for samples at pressures other than 933 mbar. Unfortunately, in practice, this does not hold true. A plot of raw and corrected instrument responses obtained experimentally (Figure 6) reveals that the relationship is somewhat linear over a narrow pressure range, but becomes fairly nonlinear over a broader pressure range (933 mbar to 150 mbar). The relationship over this broader range is more accurately described by a second order polynomial equation. For the given concentration of nitric oxide, the following polynomial relationship has been established between raw instrument response (R) and sample pressure (P):

$$R = [-9.59 \times 10^{-6} \text{ ppm/(mbar)}^2]P^2 + [2.99 \times 10^{-2} \text{ ppm/mbar}]P + 0.55 \text{ ppm.}$$

Several reasons for this departure from linearity may be considered. Instrumental factors, such as changes in detector linearity with varying throughput, might be responsible. In addition, inter- or intra-molecular interactions may change at lower pressures, thereby resulting in different line shapes and intensities. The band shapes that result from a linear subtraction of a spectrum acquired at 150 mbar and one acquired at 933 mbar indicate a reduction in spectral line width with a reduction in pressure, supporting the above theory.

Aperture Study

Factors, such as beam diameters, and the quality and alignment of optical components can affect the resolution of FTIR spectrometers.¹³ It has been demonstrated in the pressure study, that variations in spectral line widths can effect the accuracy of the system. An aperture study was undertaken to determine the relationship between instrumental resolution and the performance of the analyzer. To determine the effect of aperture size (beam diameter) on the accuracy of the nitric oxide analysis, instrument response was monitored for several aperture settings. Adjustments of the diaphragm aperture are controlled by a stepper motor. Aperture size can be changed by selecting the number of steps the motor undergoes relative to a zero point. This mechanism is very reproducible, but the relationship between motor steps and aperture area is not a linear one. Spectra were acquired at three stepper motor setting: 30, 40, and 50 steps, which correspond to aperture areas of approximately, 0.30, 0.52, and 1.27 mm²,

respectively. (The increase in throughput at a setting of 50 steps prompted the use of a 50% transmitting, neutral density filter to prevent saturation of the detector). A plot of instrument response as a function of aperture area is presented in Figure 7. A linear regression was performed on these data, and it was established that the relationship between instrument response and aperture area is linear for the given concentration of nitric oxide, for the range of aperture areas studied (slope = -1.85 ppm/mm^2 , intercept = 21.0 ppm , and a correlation coefficient = 0.998). In addition, the linear subtraction of a spectrum acquired using an aperture setting of 30 from a spectrum acquired using a setting of 50 was performed. The resultant band shapes indicate loss of resolution with increasing aperture setting.

Conclusions

The quantitative capabilities of this FTIR emissions analyzer are based on the use of high resolution infrared spectroscopy. Therefore, variations in spectral line widths may affect the accuracy of the system. A study investigating the extent of such effects on the accuracy of the nitric oxide analysis was performed. It was determined that linear equations can be used to describe the relationships between instrument response and parameters such as sample temperature and aperture area over the ranges studied. On the other hand, the relationship between instrument response and sample pressure is somewhat nonlinear over the pressure range studied. For narrower pressure ranges the relationship can be described using linear equations.

It has been determined from this work, that ambient temperature fluctuations do not appreciably alter spectral line widths. Variations in sample temperature of $\pm 10^\circ\text{F}$ are expected to result in inaccuracies on the order of $\pm 2\%$ for samples containing nitric oxide levels similar to those used in this study. If accuracies greater than $\pm 2\%$ are needed, the regulation of sample temperatures should be considered.

It has also been determined, that ambient pressure fluctuations measurably alter the widths of NO absorption lines. Variations in sample pressure of $\pm 50 \text{ mbar}$ result in errors on the order of $\pm 3\%$ for samples containing lower levels of nitric oxide. Feed back circuitry has been used successfully in this laboratory to regulate the sample pressures during vehicle testing, and is recommended if system accuracies greater than $\pm 3\%$ are required. For locations that have naturally low ambient pressures, correction factors, which compensate for lower sample pressures can be readily incorporated into the software.

It is apparent from this study, that the aperture size (beam diameter) has a noticeable effect on instrument resolution, and hence instrument response in the specific case studied. A maximum instrument response error of 6% for nitric oxide is observed for changes in aperture area from 0.52 mm^2 to 1.27 mm^2 . Since the changes in instrument response behave linearly over the range considered, it is conceivable that the data could be corrected for the variations in aperture size. However, to eliminate the effects of loss of instrument resolution due to beam diameter fluctuations, it is strongly recommended that the resolution of the reference spectra and the sample spectra be matched as closely as possible, and that aperture size remain constant.

The results of this study indicate that routine variations in parameters, such as instrument resolution, sample temperature and pressure have minimal effects on the accuracy of the FTIR analysis of low concentrations of nitric oxide. Studies that may further clarify these effects for nitric oxide, as well as for several other emission components, are in progress.

Acknowledgement

The prototype instrumentation developed in this laboratory was commercialized in 1988 by Mattson Instruments, Inc., Madison WI. This instrumentation may be further developed, in the near future, by another manufacturer.

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Table I. Spectral regions used for quantitative analysis of some exhaust components.

Component	Spectral Region (cm ⁻¹)
carbon monoxide	2010 - 2220
nitric oxide	1800 - 1940
nitrogen dioxide	1580 - 1630
nitrous oxide	2185 - 2220
sulfur dioxide	1330 - 1385
methane	1240 - 1345

Table II. Real-time detection limits of the FTIR analyzer

Component	Detection Limit (ppm)	Bags 1 or 3 (1) (mg/mile) 700 CFM	Bag 2 (2) (mg/mile) 700 CFM	Cold/Hot (3) (mg/mile) 700 CFM
CH ₂ O (Formaldehyde)	0.54	2.6	2.0	2.3
CH ₃ OH (Methanol)	1.8	9.1	6.9	8.0
CO (Carbon Monoxide)(4)	8.9	39	30	34
CO ₂ (Carbon Dioxide)(4)	470	3.2E+03	2.5E+03	2.9E+03
SUM_HC(5)	19 ppmC	42	32	37
SUM_NOX(6)	3.6 ppmN	23	17	20
NO (Nitric Oxide)	0.39	1.6	1.2	1.4
NO ₂ (Nitrogen Dioxide)	2.8	18	13	15
N ₂ O (Nitrous Oxide)	0.10	0.7	0.5	0.6
HONO (Nitrous Acid)	2.4	16	12	14
CH ₄ (Methane)	1.7	4.2	3.2	3.7
C ₂ H ₂ (Acetylene)	0.62	2.5	1.9	2.2
C ₂ H ₄ (Ethylene)	1.3	5.6	4.2	4.9
C ₂ H ₆ (Ethane)	0.54	2.6	2.0	2.3
C ₃ H ₆ (Propylene)	4.2	28	21	24
iC ₄ H ₈ (Isobutylene)	1.3	11	8.7	10
1,3-C ₄ H ₆ (1,3-Butadiene)	1.8	15	12	14
HCHO (nonspeciated HC)(5)	5.7 ppmC	12	10	11
CH ₃ CHO (Acetaldehyde)	3.6	25	19	22
C ₂ H ₆ O (Ethanol)	0.62	4.5	3.4	3.9
HCOOH (Formic Acid)	0.39	2.8	2.2	2.5
SO ₂ (Sulfur Dioxide)	0.73	7.4	5.6	6.5
H ₂ O (Water)	3200	9.0E+03	6.9E+03	7.9E+03
HCN (Hydrogen Cyanide)	0.44	1.9	1.4	1.6
NH ₃ (Ammonia)	0.85	2.3	1.7	2.0
CF ₄ (Carbon Tetrafluoride)	6.4E-03	8.8E-02	6.8E-02	7.8E-02

(1): Limits for UDDS cold start transient phase (Bag 1) or the hot start transient phase (Bag 3) at a dilution flow rate of 700 CFM.

(2): Limits for UDDS cold start stabilized phase (Bag 2) for a dilution flow of 700 CFM.

(3): Limits for the Cold/Hot calculation for a dilution flow rate of 700 CFM.

(4): Ranges appropriate for atmospheric levels provide greater sensitivity for these components.

(5): Molecular weight based on a hydrogen to carbon ratio of 1.85:1.

(6): Based on the molecular weight of NO₂.

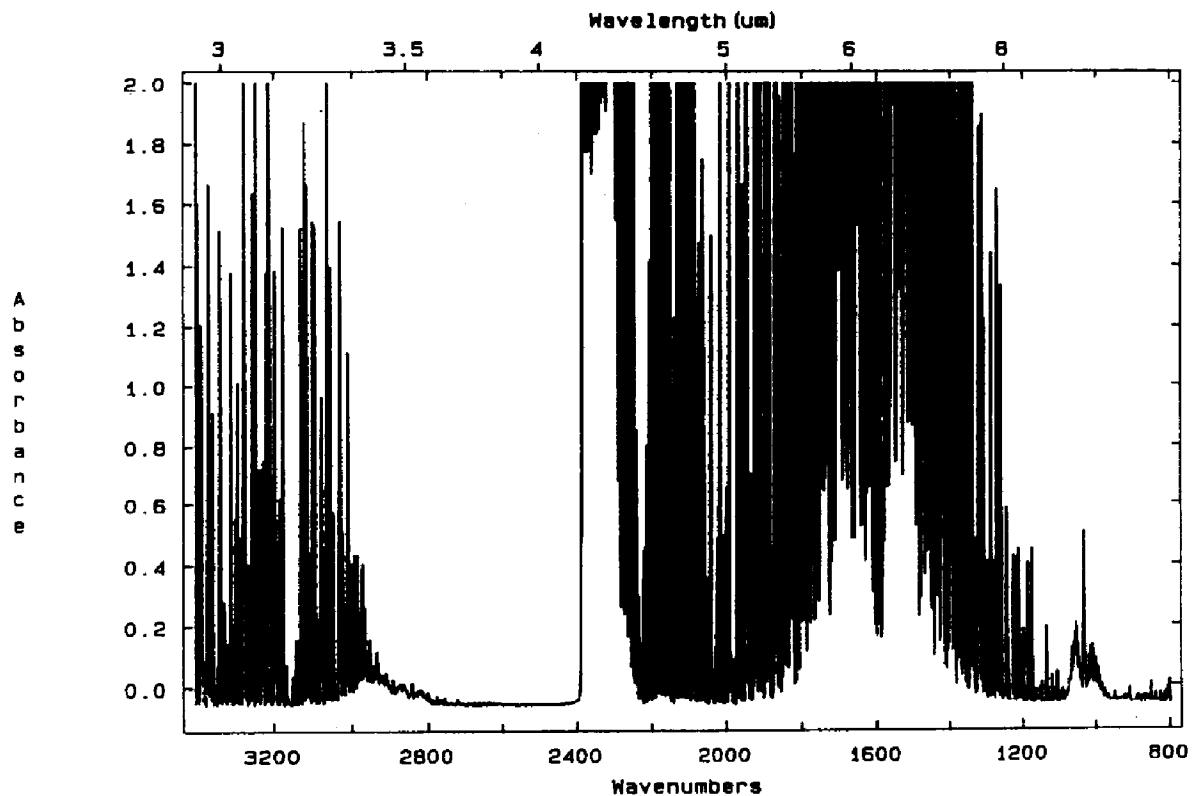


Figure 1. High resolution spectrum of dilute vehicle exhaust from an alternate fuel vehicle running on a mixture of 85% methanol and 15% gasoline.

Methane Emissions / Post-Catalyst Temperature Gasoline Fuel

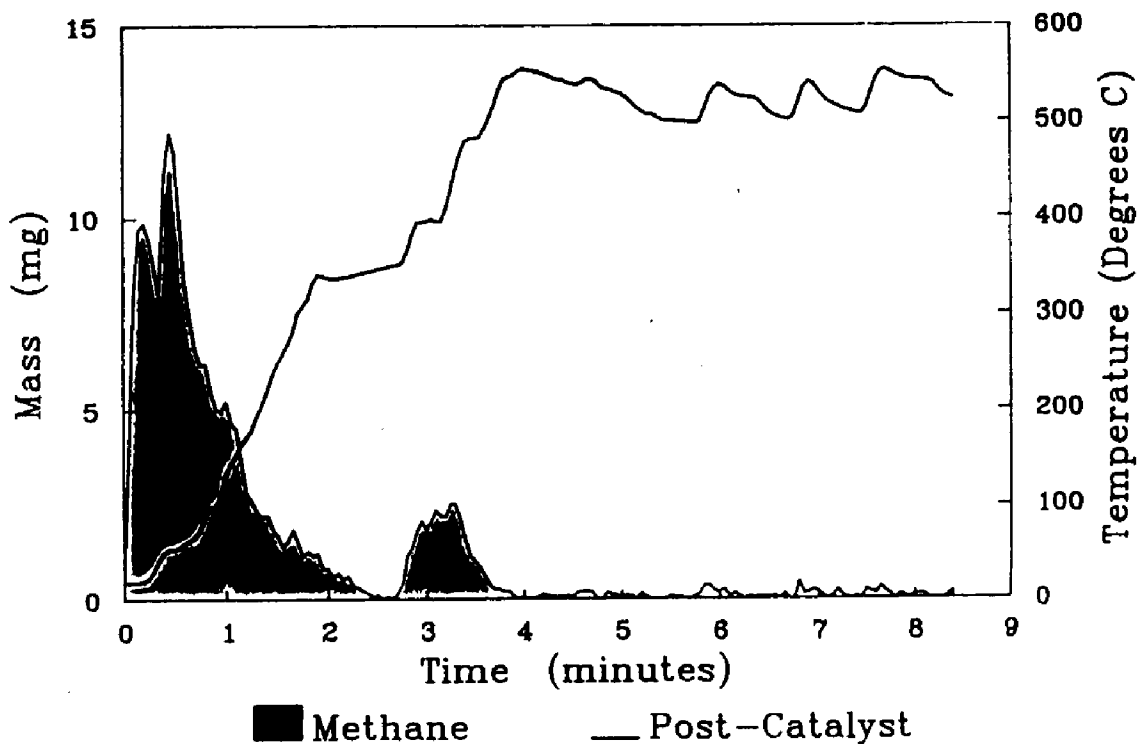


Figure 2. Methane emissions and catalyst temperature as a function of time for a gasoline fueled vehicle during the cold start transient phase (Bag 1) of the Urban Dynamometer Driving Schedule (UDDS).

Formaldehyde Emissions for Bag 1

M-85 Fuel

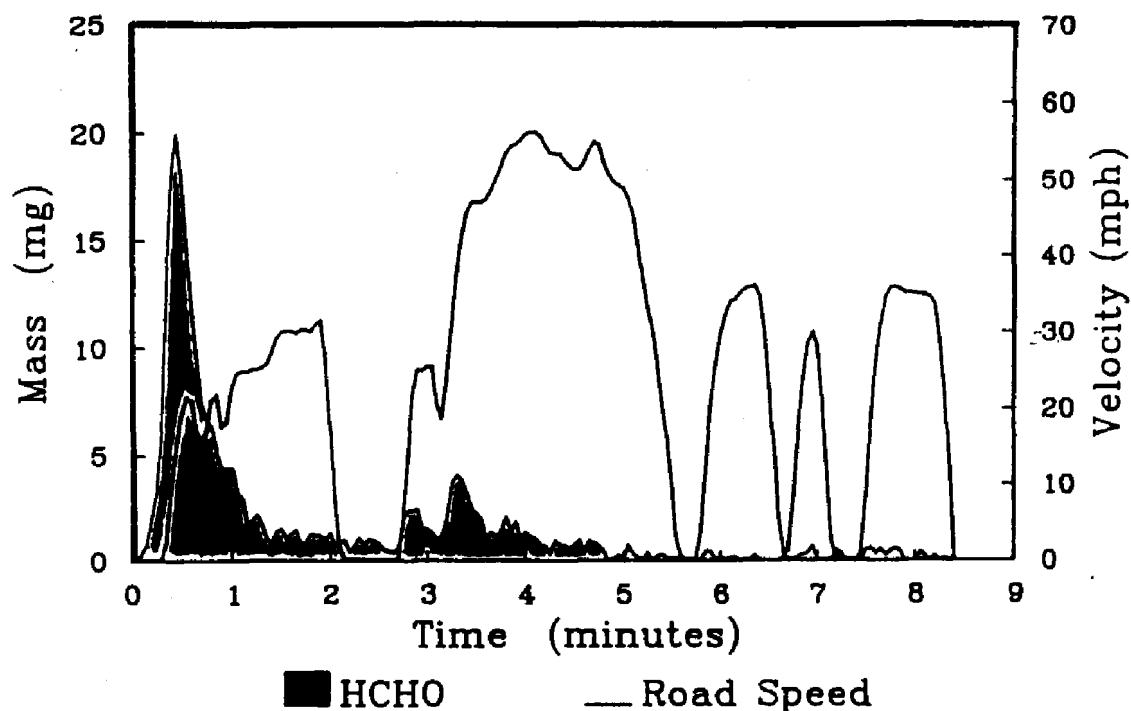


Figure 3. Formaldehyde emissions and road speed as a function of time for an alternative fuel vehicle running on 85% methanol and 15% gasoline during Bag 1 of the UDDS.

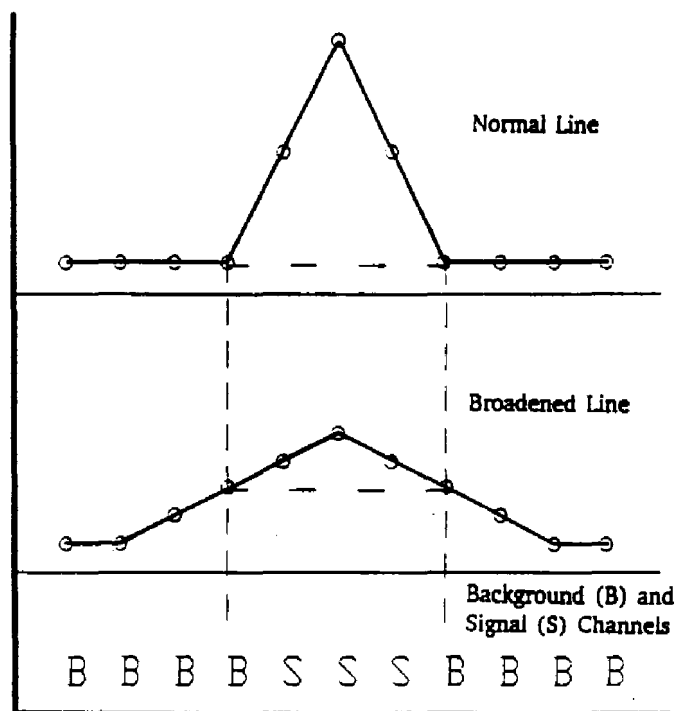
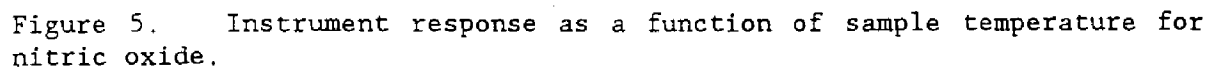


Figure 4. The effect of a variation in the spectral line width on the accuracy of the masking technique.

Nitric Oxide



Nitric Oxide

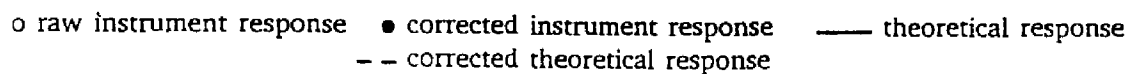


Figure 6. Instrument response as a function of sample pressure for nitric oxide.

IRIS STUDY
Nitric Oxide

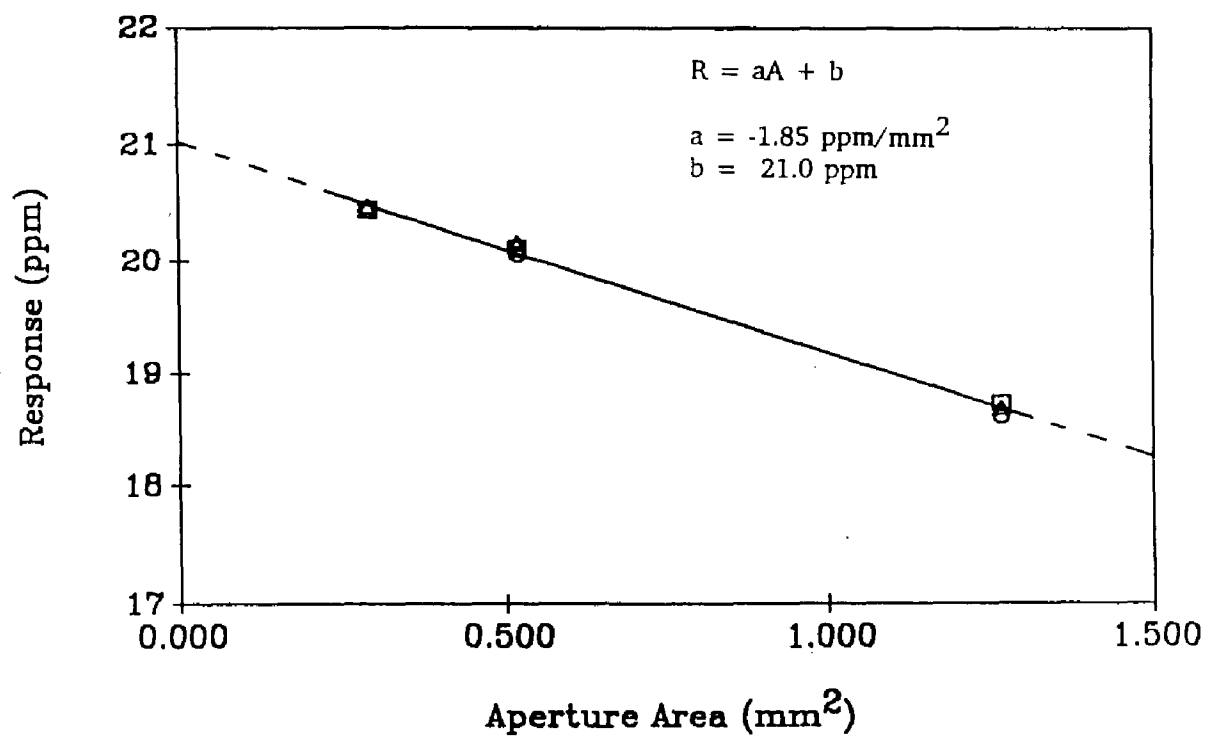


Figure 7. Instrument response as a function of aperture area for nitric oxide.

EMISSIONS FROM A FLEXIBLE-FUELED VEHICLE

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In anticipation of a shift from gasoline to methanol, flexible-fueled automobiles capable of operating on various mixtures of both fuels are being developed. This study examines both the exhaust and evaporative emissions from a prototype General Motors Variable Fuel Corsica. Results are reported for tests conducted at temperatures of 40°, 75°, and 90°F, and for fuels MO, M25, M50, M85, and M100. In addition to regulated emissions and fuel economy, emission rates for methanol, aldehydes, and a large number of hydrocarbon compounds were measured. The data indicate that as fuel methanol content is increased, formaldehyde and methanol comprise increasingly greater portions of the organic material while hydrocarbons comprise less. Increasing fuel methanol content has no significant effect on exhaust regulated emission rates (organic material, carbon monoxide, and nitrogen oxides) nor on the composition of total hydrocarbons, except for methane, which increases substantially. The effect of ambient temperature on both exhaust and evaporative emissions is similar to its effect on gasoline cars: organic and carbon monoxide exhaust emissions increase substantially at the lower temperatures, and evaporative emissions increase steadily with increases in temperature.

INTRODUCTION

The lack of progress toward attainment of the ambient ozone standard has prompted many areas of the country to press for stricter emission standards and other abatement strategies. In Southern California, regional officials have voted for a plan that would, by 1998, convert 40% of the cars to cleaner fuels. If enacted, the plan would ban the use of conventional gasolines in Southern California by 2007.

Currently, the most promising alternative fuel for automobiles appears to be methanol. In anticipation of a fuel switch to methanol, some automobile companies have already developed vehicles which are designed to operate on methanol and/or gasoline. One scenario suggests that these flexible-fuel cars could proliferate during a transition of fuels to comprise a significant fraction of the consumer fleet. For this reason, a study was undertaken to characterize both the exhaust and evaporative emissions from a flexible-fuel automobile. The data obtained in this study will be used in air quality models to predict the impact of methanol usage on ambient ozone levels.

EXPERIMENTAL PROCEDURES

Test Vehicle

The test vehicle used in this study was a 1988 General Motors (GM) Variable Fuel Corsica having a conventional, closed loop, three-way catalyst. Its engine is a port fuel injected, 2.8-l six-cylinder configuration, having a compression ratio of 8.9:1. A fuel sensor electronically monitors the oxygen content of the fuel being injected to continuously adjust engine parameters, enabling optimum operation with respect to fuel alcohol content.

The Variable Fuel Corsica was obtained on loan from the GM Advanced Engineering Staff (AES) to EPA for testing. Prior to delivery, the Corsica was tested for both exhaust and evaporative regulated emissions by GM. Much of these data are included in the paper for comparative purposes when regulated emissions data are presented.

Fuel Description

The five fuels examined in this study were M0, M25, M50, M85, and M100. In these five descriptors, the prefix "M" is followed by a number representing the volume percent of methanol mixed with gasoline. For example, an M85 fuel contains 85% methanol and 15% gasoline. The methanol used was of a laboratory grade specification and the gasoline with which it was mixed was indolene, the standard certification fuel. The Reid vapor pressures (RVP) measured for the M0, M25, M50, M85, and M100 fuels were 9.0 psi, 10.9 psi, 10.1 psi, 8.0 psi, and 4.6 psi, respectively.

Facility Description and Emission Measurement

All tests were conducted at the EPA Environmental Research

Center Annex, Research Triangle Park, North Carolina. The chassis dynamometer used for vehicle road load simulation is enclosed within a temperature controlled test chamber (TCTC), which permits vehicle soak and operation at temperatures ranging from 20°F to 100°F.

Emissions were examined for both regulated (organic material (OM), carbon dioxide (CO), and nitrogen oxides (NOx)) and unregulated pollutant emissions. Regulated emissions were measured using the procedures set forth in the Federal Register (1). Nonregulated pollutants, consisting of aldehydes and speciated hydrocarbons, were measured using methods previously published (2,3).

Run Schedule and Test Descriptions

The overall test program was broken down into test sets and subsets. The sets consisted of all runs with a given test fuel, and the subsets were all runs at a given test temperature. Because there were five fuels being examined, there were a total of five test sets which were run in the order of M0, M85, M100, M50, and M25. There were three subsets run in the order of 75°F, 40°F, and 90°F, and three replicate tests were run within each subset. The subset for M100 at 40°F was not run because the vehicle could not be cold started on M100 at temperatures below 60°F.

RESULTS AND DISCUSSION

Exhaust Emissions

Exhaust emission results are presented in Table 1. These presentations enable emission rate comparisons for the two principal variables examined in the study: fuel methanol content and ambient temperature.

Emission rates, except for NOx, are significantly higher at the lowest temperature examined (40°F). This is expected because organic and CO emissions typically increase as ambient temperature decreases. In a similar study involving a dedicated methanol car (4), the increases in HC, CO, and methanol emissions were even more pronounced than those presented here with M85 fuel.

The effect of fuel type (fuel methanol content) on CO, NOx, and total organic exhaust emission rates is not significant; however, fuel type does strongly influence the composition of organic material. Increases in fuel methanol content result in increases in methanol and formaldehyde emission rates with corresponding decreases in HC emission rates. In addition to these compositional changes, hydrocarbon compositions are also affected. As fuel methanol content is increased, steady but significant increases in the methane fraction occur.

The fractions of hydrocarbon compounds other than methane are much less sensitive to either fuel methanol content or ambient temperature. Table 2 provides fractions as percentages for 6 of the more important hydrocarbon compounds contained in

exhaust emissions. The final column in the table gives average values from recent exhaust emission studies conducted with gasoline vehicles (5,6). In general, the hydrocarbon composition from gasoline vehicle exhaust emissions appears similar to those from the flexible-fuel vehicle, except for methane, as discussed above.

An additional formaldehyde measurement was made during the first 125 s of the test to determine the portion of formaldehyde emissions occurring immediately after the cold start. Formaldehyde emissions, which occur during the cold transient test phase (first 505 seconds), generally comprise a vast majority of the total test formaldehyde emissions. Table 3 reports the emission rates and percentages of formaldehyde emitted during the first 125 s and the first 505 s of operation.

Evaporative Emissions

Evaporative emission summaries are presented in Table 3. As expected, evaporative emissions increase with increase in either test temperature or fuel volatility. For the 90°F tests, the order of increasing evaporative emission rates corresponded precisely with order of increasing fuel volatility: M100 < M85 < M0 < M50 < M25.

CONCLUSIONS

Results obtained in this study support the following conclusions:

1. Regulated exhaust emissions increases at 40°F are comparable to increases observed for gasoline vehicles.
2. Methanol and formaldehyde exhaust emission rates increase substantially at 40°F relative to the 75°F tests.
3. Regulated exhaust emission rates (OM, CO, and NOx) are not significantly affected by fuel methanol content.
4. As methanol content increases, the hydrocarbon portion of the organic mass decreases while the methanol and formaldehyde portions increase.
5. The methane fraction of exhaust hydrocarbons increases with increase in fuel methanol content. Other hydrocarbon compound fractions are less sensitive to fuel methanol content and are similar to values reported from gasoline engine studies.
6. More than half of the FTP formaldehyde emissions occur during the first 125 s of the test with M85 and M100 fuels.
7. Total organic evaporative emissions increase with increase in test temperature and with increase in fuel volatility.

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Table 1. Exhaust emissions

	OMHCE (g/mi)	HC (g/mi)	MeOH (g/mi)	HCHO (mg/mi)	CO (g/mi)	NOx (g/mi)
M0						
40 F	0.92	0.92	0.00	5.6	8.80	0.20
75 F	0.32	0.32	0.00	4.8	2.60	0.22
90 F	0.36	0.36	0.00	4.7	2.80	0.26
M25						
40 F	0.78	0.70	0.18	13.0	8.46	0.22
75 F	0.28	0.22	0.11	8.8	2.50	0.24
90 F	0.30	0.25	0.11	7.1	3.60	0.26
M50						
40 F	0.67	0.47	0.44	23.2	7.50	0.24
75 F	0.27	0.17	0.21	14.1	2.90	0.26
90 F	0.25	0.15	0.20	12.9	3.00	0.24
M85						
40 F	1.00	0.35	1.45	58.0	8.50	0.28
75 F	0.24	0.11	0.29	27.3	2.60	0.26
90 F	0.32	0.17	0.31	28.5	2.40	0.31
M100						
75 F	0.42	0.04	0.82	40.6	3.10	0.27
90 F	0.31	0.03	0.60	31.7	3.10	0.24

notes: (a) Organic=HC+13.8/32(MeOH)+13.8/30(HCHO)
(b) no 40 F M100 tests.

Table 4. Evaporative emissions

	OMHCE (grams)	HC (grams)	MeOH (grams)
M0			
40 F	0.45	0.45	0.00
75 F	0.82	0.82	0.00
90 F	1.45	1.45	0.00
M25			
40 F	0.56	0.47	0.20
75 F	1.45	1.34	0.26
90 F	5.38	4.83	0.62
M50			
40 F	0.25	0.17	0.19
75 F	0.58	0.46	0.28
90 F	1.67	1.47	0.43
M85			
40 F	0.28	0.17	0.16
75 F	0.64	0.48	0.25
90 F	0.65	0.50	0.31
M100			
75 F	0.40	0.12	0.58
90 F	0.47	0.10	0.85

notes: (a) Organic=HC+13.8/32(MeOH)
(b) no 40 F M100 tests.

Table 2. Fractions for six selected exhaust HC compounds. (% of total HCs)

	Test Temp (F)	M0	M25	M50	M85	M100	20 gas vehicles
METHANE	40	10	10	11	15		
	75	10	12	15	25	50	17
	90	13	13	17	19	56	
ETHYLENE	40	5	5	5	5		
	75	5	6	6	5	1	5
	90	5	5	5	4	2	
PROPYLENE	40	3	3	3	2		
	75	4	4	4	3	0.5	2
	90	4	4	4	2	0.0	
BENEZENE	40	3	3	3	3		
	75	3	3	3	3	0.7	4
	90	3	3	3	3	1.5	
TOLUENE	40	14	14	15	14		
	75	14	14	12	12	2.0	9
	90	13	11	12	12	3.0	
1,3-BUTADIENE	40	0.3	0.6	0.4	0.2		
	75	0.5	0.6	0.6	0.4	0.0	0.3
	90	0.4	0.6	0.8	0.6	0.0	
THC (g/mi)	40	0.9	0.7	0.5	0.3		
	75	0.3	0.2	0.2	0.1	0.02	
	90	0.3	0.3	0.2	0.1	0.01	

Table 3. Percent of FTP formaldehyde emission at 125 s. and 505 s.

	Amb. Temp. (F)	% Total	
		125 s.	505 s.
M85	40	51	81
	75	59	88
	90	51	85
M100	75	60	92
	90	63	90

A RETROSPECTIVE ANALYSIS OF A BASELINE AIR PATHWAY
ASSESSMENT AT A PRE-REMEDIAL SUPERFUND SITE

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A Baseline Air Pathway Assessment (APA) was performed at a Pre-Remedial Superfund Site containing surface and subsurface chemical contamination. The objectives of the baseline APA were to: 1) measure the average upwind and downwind concentrations of selected VOCs at the 95% confidence level in the ambient air around the site and compare these concentrations to the Applicable, Relevant, and Appropriate Requirements (ARARs) established for this project; 2) determine whether the site is a source of the VOCs measured in ambient air based on statistically significant differences at the 95% confidence level between average upwind and downwind concentrations; and 3) measure average concentrations of selected VOCs at the 95% confidence level within selected dwellings and compare these concentrations to the ARARs established for the project. A Quality Assurance Project Plan (QAPP) was developed describing the strategy and procedures used to perform the APA. The project was implemented, whole air samples were collected and analyzed, the data were assessed, and a report was prepared. This paper describes and evaluates the study and discusses alternate approaches for performing data analysis using the pollutant and weather data obtained during the study.

INTRODUCTION

A Superfund site containing a variety of stored chemicals and both surface and subsurface soil contamination was investigated to determine whether there was an ongoing air release. The investigation consisted of performing a baseline APA utilizing air monitoring procedures. A statistically significant number of samples (6) were collected at each site comprising the monitoring network around the site perimeter. Another set of six samples were collected in crawl spaces of nearby houses to determine if volatile organics were being emitted in soil gas resulting from subsurface contamination around the site. Summa^R polished spheres with flow control valves were used to collect the samples, which were then analyzed by Gas Chromatography/ Matrix Isolation-Fourier Transform Infrared Spectroscopy.

Sample results were grouped by sampling location in relation to the wind, and averaged. The averages of the grouped results were then statistically compared to determine if measured VOC concentrations were significant.

EXPERIMENTAL METHODS

The study plan contained an air monitoring network which was designed so that the monitoring sites would be located upwind and downwind of the site according to the current and predicted wind conditions. The network consisted of one upwind monitoring station and three downwind monitoring stations all of which were located near (but outside of) the site fenceline. The downwind monitoring stations were located directly downwind and at 45° right and left of the downwind monitoring station. Sampling periods were limited to four hours due to sampling equipment constraints. In order to average out diurnal effects and other variables which may cause short term concentration fluctuations, multiple 4 hour sampling events were performed with the individual events collected over different periods of a 24 hour cycle. A total of six sampling events were performed. An on-site meteorological station was used to measure wind direction and velocity. A sampling event was considered valid only if the actual wind direction was appropriately aligned with the monitoring network for a minimum of 70% of the 4 hour event. If the winds did not meet this criteria, the samples were voided and the event repeated.

Sampling operations began on August 17, 1989, and were completed on September 19, 1989. Collected samples were prepared for analysis by cryogenic preconcentration with qualitative and quantitative analysis accomplished using Gas Chromatography/ Matrix Isolation-Fourier Transform Infrared Spectroscopy/Flame Ionization Detection (GC/MI-FTIR/FID). The samples were analyzed for 17 target VOCs. The measured average concentrations from each site within the monitoring network were compared to the Applicable, Relevant, and Appropriate Requirements (ARARs) contained in the Quality Assurance Project Plan (QAPP). The ARARs for this project were based on the

American Conference of Governmental and Industrial Hygienists' (ACGIH) Threshold Limit Values (TLVs) for the respective VOCs reduced by a factor of 1/420.

RESULTS

The ambient air results showed only 1,1,1-trichloroethane, trichloroethylene, methylene chloride, and tetrachloroethylene at concentrations above the Method Detection Limits (MDL). The mean concentrations and bounding 95% confidence limit at each monitoring site were statistically compared to the ARARs and to one another. This was done using the student t test for the predicted upwind, downwind, downwind 45° right, and downwind 45° left, sites. Statistically, both methylene chloride and tetrachloroethylene were at the same concentration at all monitoring sites. Using this same test, 1,1,1-trichloroethane was detected at a higher concentration 45° downwind left and downwind center than upwind. Trichloroethylene was detected at a statistically higher concentration 45° downwind left than upwind (Figure 1-4). Both 1,1,1-trichloroethane and trichloroethylene were below their respective ARARs at the 95% confidence level.

The three nearby residences were sampled with six samples collected from each crawl space. All crawl space samples were collected from 8:00 am to 4:30 pm. Methylene chloride, cis-1,2-dichloroethylene, hexane, 1,1,1-trichloroethane, trichloroethylene, toluene, and tetrachloroethylene were found above the MDLs. The average concentrations for each residence was compared against the average blank value at the 95% confidence level. There was no significant difference between the blank concentrations and the concentrations found in the crawl spaces.

ALTERNATE DATA ANALYSIS PROCEDURE

An analysis of the data was performed using the monitoring data from the actual downwind rather than the predicted downwind. This approach uses the predicted downwind site (i.e. network centerline site) for the 1st and 6th event and the 45° left site for the remaining data points. The mean concentration was calculated using the individual concentrations measured from the sites.

A plot of the actual downwind VOC concentrations vs the sampling time (Figure 5) shows that during daylight hours the concentrations are significantly higher than at night. Two possible causes were identified. One cause could be increased daytime emissions from the contaminated soil on-site which was found to contain trichloroethylene and tetrachloroethylene. The higher daytime concentrations could result from higher soil temperatures causing the soil to de-gas at a higher rate during the daytime hours. The higher daytime concentrations could also have been from emissions within an on-site building

(chemical storage warehouse) where a cleanup effort was going on during daylight hours. Probably, the higher daytime values were caused by a combination of both possibilities.

In order to determine if the increased concentrations were the result of emissions from the building, the concentrations of airborne VOCs found within the building were compared to concentrations found in the soil, at the downwind site perimeter, and in the crawl spaces (Figure 6). Trichloroethylene is the highest of the VOC in both building samples, the downwind sample and the residence. Benzene, 1,1,1-trichloroethane and toluene concentrations varied for second highest VOC in the building samples, the downwind sample and the residence. Methylene chloride concentration was always the lowest. This fact coupled with the fact that the warehouse doors were only open in the daytime could explain the higher daytime ambient air concentrations.

The total VOC concentrations were also then plotted along with the days in which rain fall occurred. (Figure 7 & 8). This appears to show that the rain had little effect on the emissions.

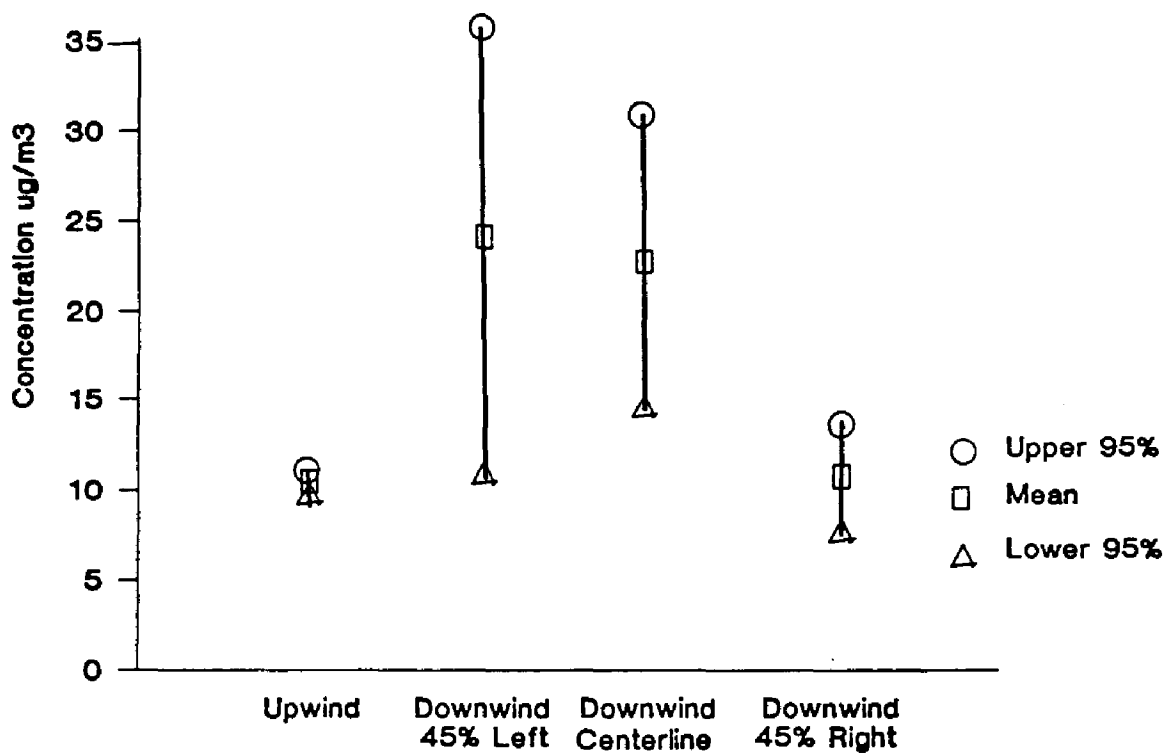
CONCLUSION

Use of the data analysis procedures contained in the project QAPP were appropriate to: 1) determine if VOCs were leaving the site and at what concentration; 2) measure concentrations of VOCs in the crawl spaces; and 3) determine whether the project ARARs were exceeded. Use of alternative techniques of data analysis were effective in obtaining additional information which facilitates an understanding of various factors affecting the ambient air concentrations around the site.

REFERENCES

1. J. Hudson, "Quality Assurance Project Plan For Air Toxics Monitoring at ..., U.S. Environmental Protection Agency, Region VII.
2. R. Tripp, "Toxic Air Monitoring in Ambient Air at ...", U.S. Environmental Protection Agency, Region VII.
3. R. Tripp, "Toxic Air Monitoring at Residences Near ...", U.S. Environmental Protection Agency, Region VII.

1,1,1- Trichloroethane



Trichloroethylene

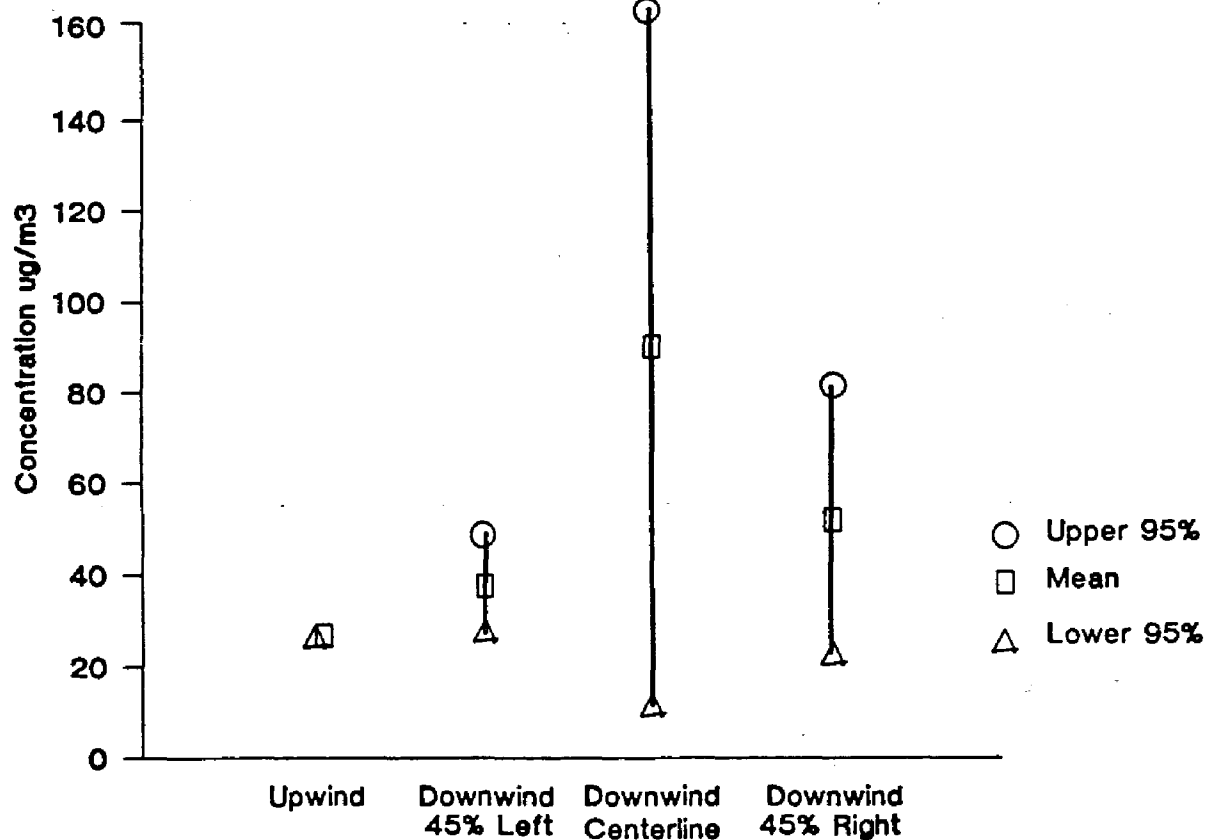
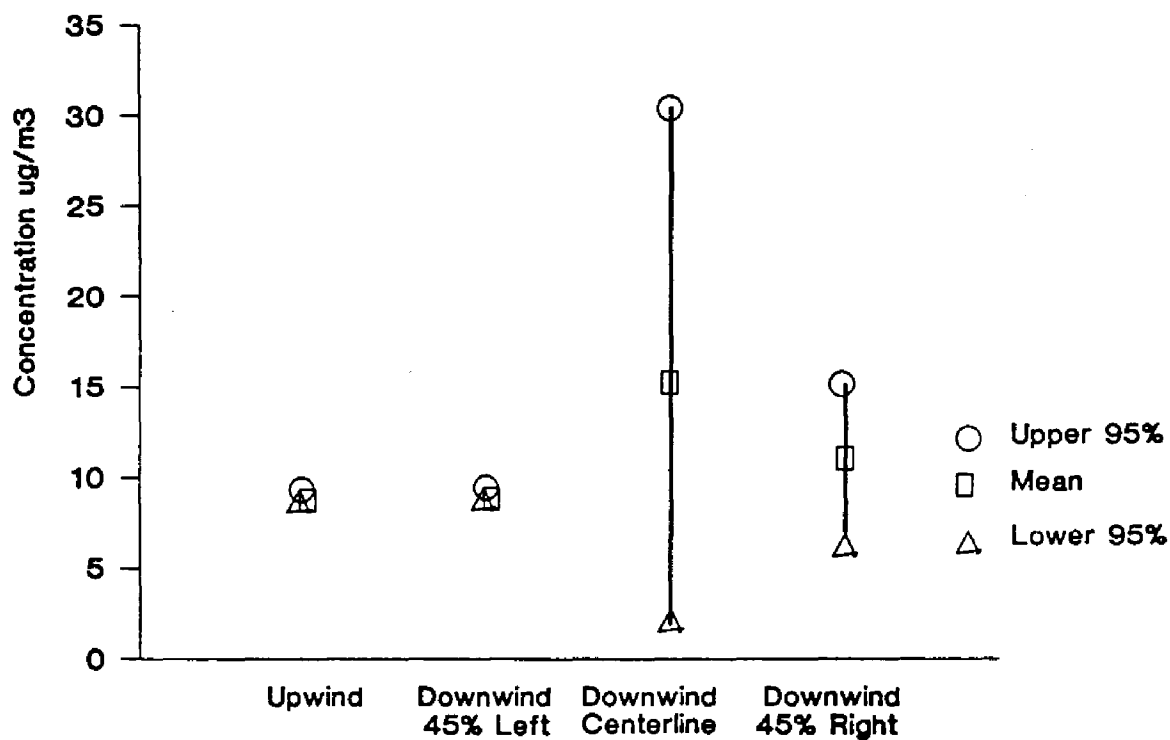


Figure 1 & 2. Statistical representation of the mean and 95% confidence level for two compounds which were reported at levels above the method detection limit.

Tetrachloroethylene



Methylene Chloride

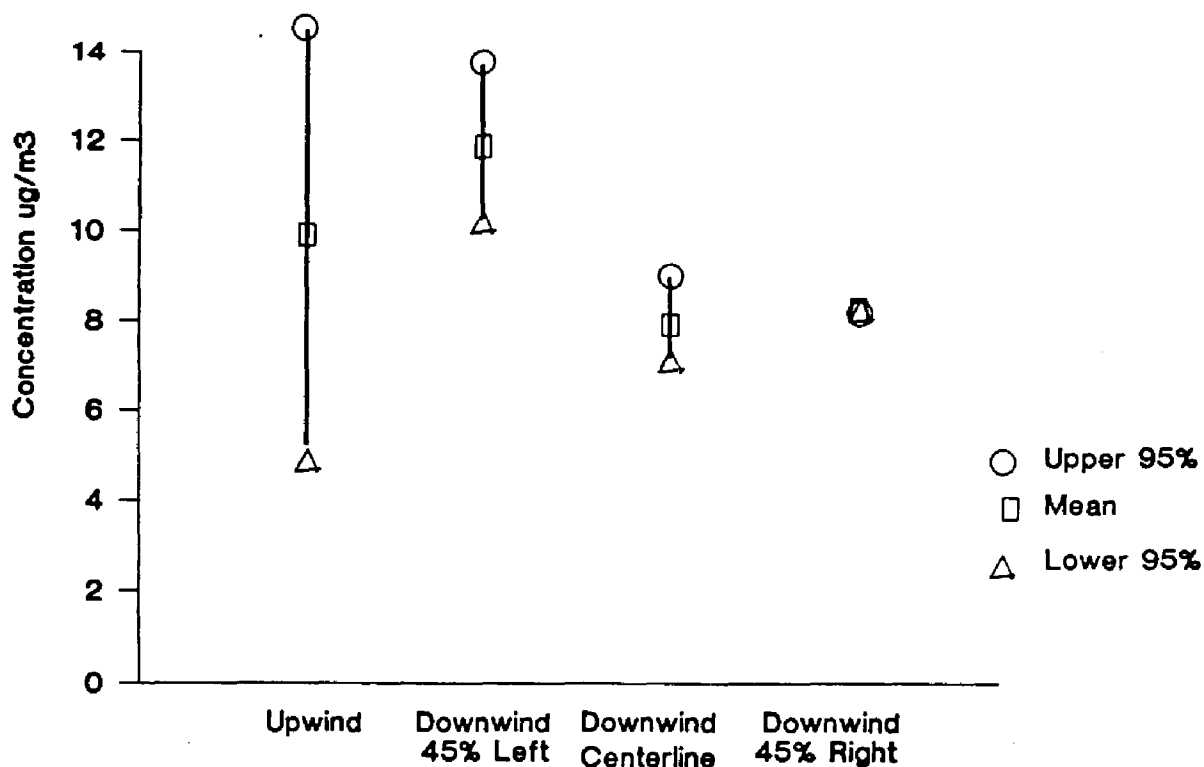


Figure 3 & 4. Statistical representation of the mean and 95% confidence level for two compounds which were reported at levels above the method detection limit.

Downwind Concentration Verses Time

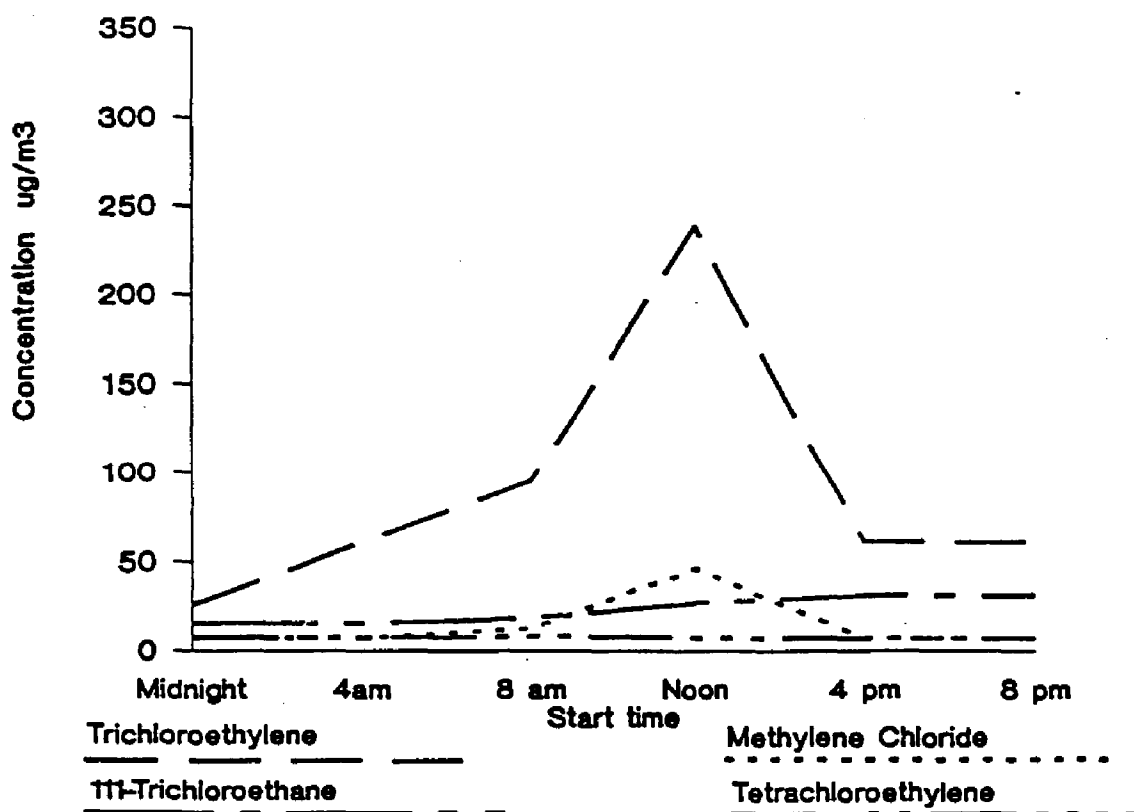


Figure 5. Concentrations of the ambient results verses time for the individual downwind site.

Comparison of Sampling Points

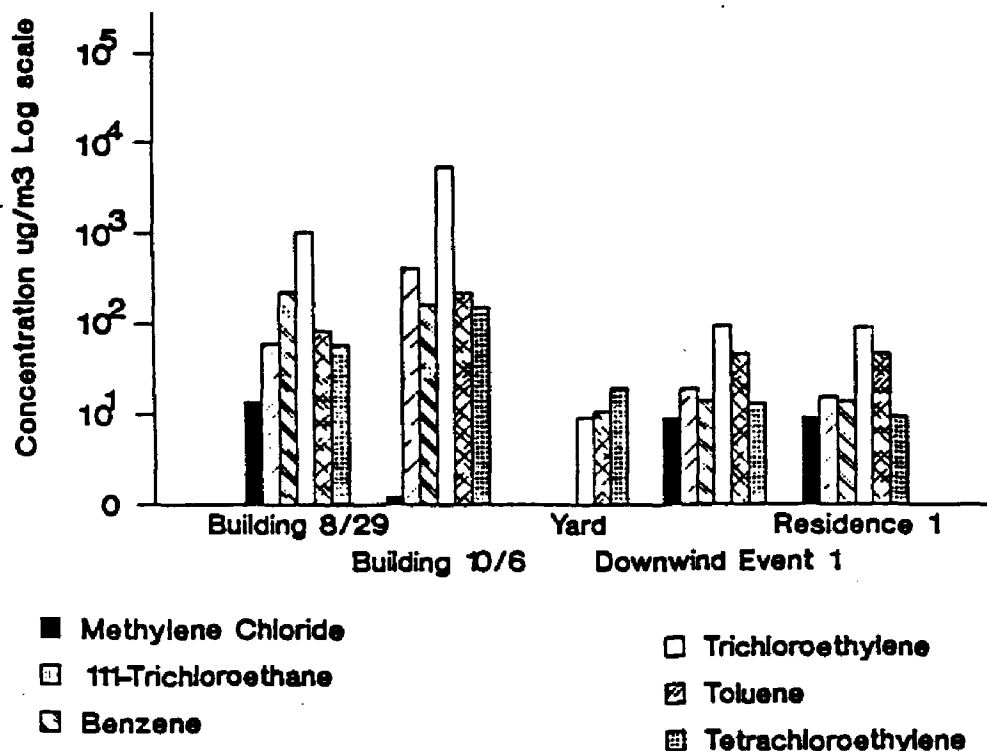


Figure 6. Comparison of the building and soil results verses the two highest events E1 & R4).

Concentration and Rain Downwind Ambient Data

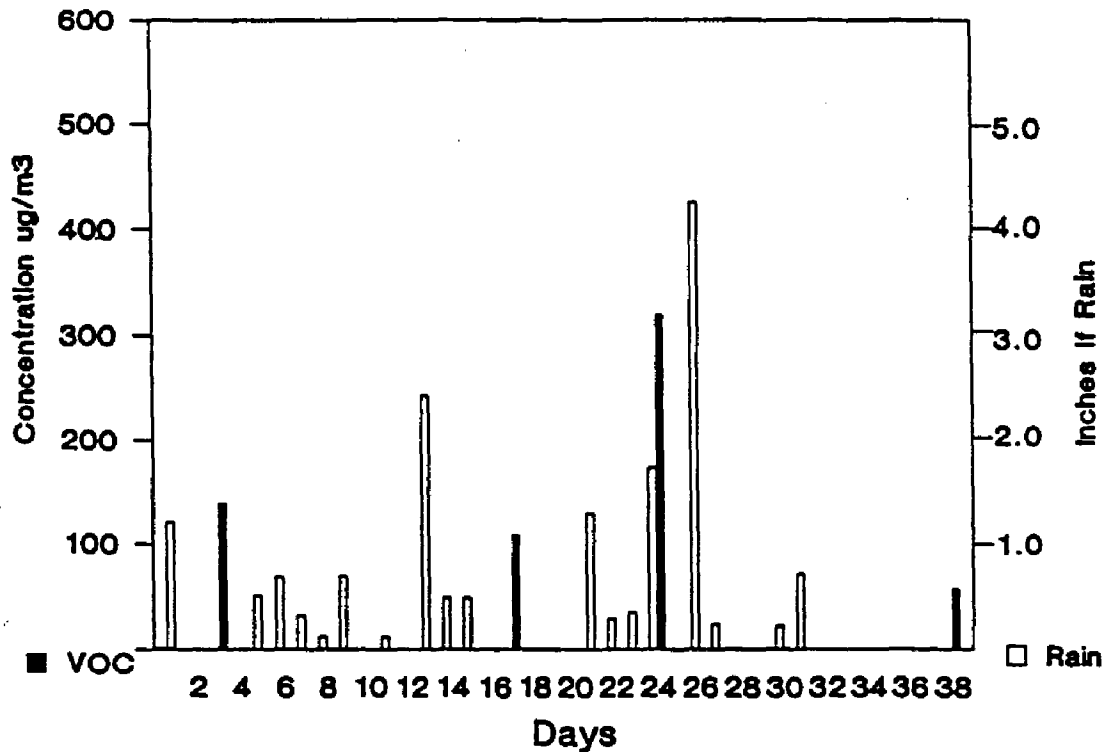


Figure 7. A comparison of the ambient VOC concentration and the amount of rain.

Concentration and Rain Residence 1

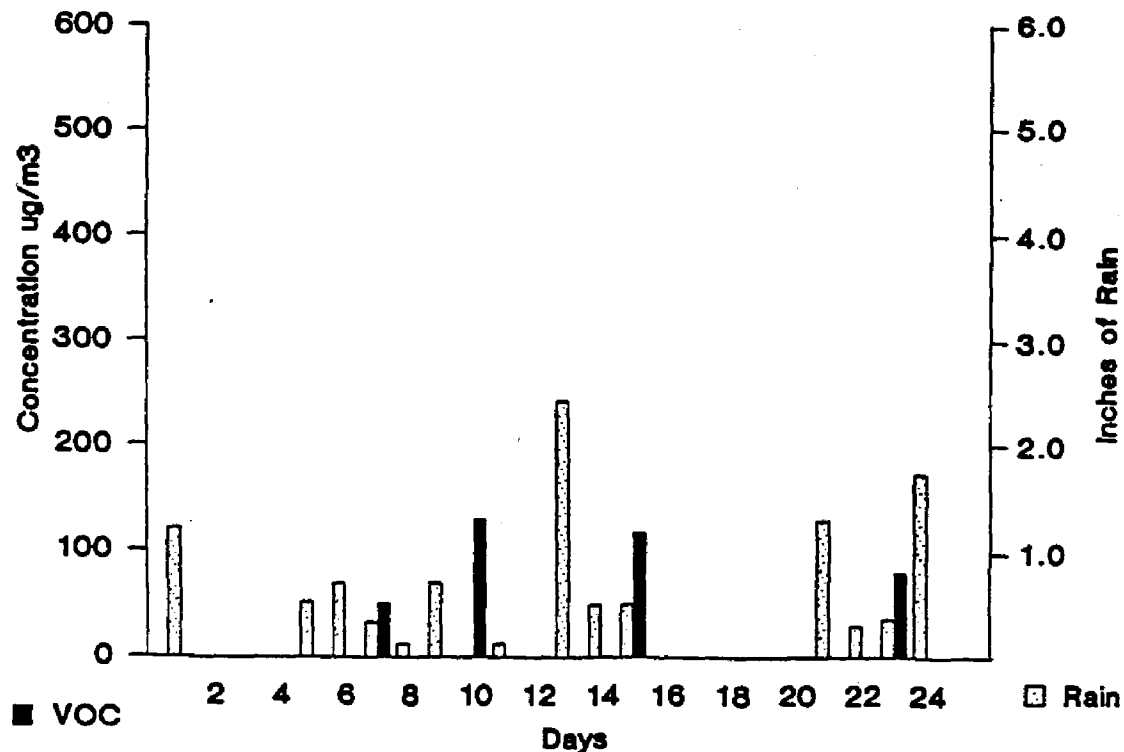


Figure 8. A comparison of the residential VOC concentration and the amount of rain.

**AMBIENT AIR MONITORING OF A SARA TITLE III
FACILITY USING THE TAGA 6000E MS/MS**

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SARA Title III legislation requires facilities to report the quantities of regulated chemicals that are used on-site in an effort to determine the chemicals' fate. One pathway by which a chemical may leave a facility is through volatilization into the atmosphere. These chemical emissions pollute the environment and may be a potential health problem. The TAGA 6000E was used to investigate a specific site for chemical losses due to volatilization by analyzing the ambient air on and off the facility's property.

Introduction

In 1986, the Emergency Planning and Community Right-to-Know Act, also known as Title III, was established. This act has four major sections, with Section 313 providing regulations for toxic chemical release reporting. Facilities subject to this reporting are required to complete Toxic Chemical Release Form (Form R) for specified chemicals. Information necessary to complete this form includes the quantity of the chemical entering air, land, and water annually.

In 1989, the Research Engineering and Analytical Contract (REAC) was directed by the US EPA Environmental Response Team (ERT) to provide analytical support to US EPA Region I in its efforts to conduct an air monitoring study in the vicinity of a Title III facility in North Haven, Connecticut. Monitoring was being conducted by Region I to determine if this facility was introducing regulated chemicals into the air. The study was designed to monitor off site locations on the perimeter of the facility for compounds whose presence in the ambient air would strongly suggest origination at the facility. The air study also included the performance of on-site analyses for compounds, to locate their sources.

Experimental Methods

Eight target compounds (Table I) were selected for continuous monitoring by the TAGA 6000E (Figure 1). Five of these compounds were selected based on their identification in the facility's Title III report. The other three compounds were selected because they represent common solvents, and because one is an indicator of target compound contribution due to vehicular exhaust. The sampling was performed during periods when it was believed that the meteorological conditions would permit observation of the maximum concentrations of the targeted compounds.

The TAGA 6000E performed direct-air sampling. Outside air was continuously drawn through a port in the roof, at a flow rate of approximately one and one-half liters per second. The sample passed over a glass splitter, where a representative sample entered the transfer line leading to the source. The remaining flow was vented from the bus.

While continuously analyzing for the target compounds, mobile monitoring was performed along public roads and over lanes around the commercial facilities surrounding the Title III plant (Figure 2). As the mobile monitoring proceeded, the computer was flagged with a letter to denote an event or a location; these flags were also recorded on the TAGA operator's log sheet. The flags are indicated on the ion profiles (Figure 3) and correspond to the map locations associated with that file. Once a plume was located, an effort to isolate the source was conducted by monitoring around the suspected source to determine if any upwind contributions existed.

Summa canisters were used as the medium to collect whole-air samples. The canisters utilized for this field activity had been cleaned and certified prior to release to the sampling crew; before any sample was collected, each canister was checked for leaks with a pressure gauge to ensure that a proper vacuum existed.

Once the TAGA identified a plume, the sampling strategy was to collect a Summa. The collection was accomplished by connecting a Summa to the TAGA sample air flow tubing via a glass splitter and a section of Teflon tubing. No attempt was made to regulate the flow rate into the canister. After the Summa had achieved ambient pressure, the valve was closed, the tubing was disconnected, and both the canister and the glass splitter were capped. The time, date, and location of sampling were noted on the canister, and also included on the TAGA operator's log sheet.

The Summas were returned to Edison, New Jersey, where their pressure was recorded; ultra-high purity nitrogen was added until the canister's final pressure was twice its initial pressure; and the canister's contents were analyzed by gas chromatograph/mass spectrometer (GC/MS) for targeted and non-targeted compounds. The Summas were also analyzed by the TAGA for the targeted compounds.

Results and Discussion

This investigation had three goals: 1) identify off site plumes using target compounds; 2)

attempt to locate the sources of plumes, using meteorological data collected concurrently with sampling; and 3) collect whole-air samples using Summa canisters for target and non-target compound analysis at a later date using conventional methods.

Sampling was conducted during periods when it was believed that the meteorological conditions would produce an atmospheric inversion, resulting in observation of maximum concentrations of target compounds. These sampling periods were:

Sampling Period I	August 8, 1989	04:29 - 07:42
Sampling Period II	August 8, 1989	20:17 - 23:52
Sampling Period III	August 9, 1989	12:34 - 16:55
Sampling Period IV	August 10-11, 1989	23:40 - 03:19

Four distinct plumes were observed off site. One contained the target compounds benzene, toluene, and chlorobenzene. This plume is believed to have originated from the Title III facility. Another plume contained the target compound 1,1,1-trichloroethane. This plume is believed to have originated from an electrical part manufacturing plant. The third plume contained methylene chloride and is believed to have originated from a parcel delivery service. The fourth plume is suspected to have originated from a graphic arts building. The maximum concentration observed off site for the target compounds were:

Benzene	300 ppb
Chlorobenzene	30 ppb
Methylene Chloride	120 ppb
1,1,1-Trichloroethane	1100 ppb
Toluene	180 ppb
Xylene	80 ppb
1,4-Dioxane	18J ppb

No 1,2-dichloroethane was detected off site. The J associated with the 1,4-dioxane concentration denotes that the value is above the detection limit but below its quantitation limit. The maximum concentration observed on-site for the target compounds were:

Benzene	5500 ppb
Chlorobenzene	350 ppb
1,2-Dichloroethane	70 ppb
Toluene	1700 ppb

No methylene chloride, 1,4-dioxane, 1,1,1-trichloroethane, or xylene was detected on-site.

REAC provided a meteorological station for the examination of the micro-meteorology at various locations near the Title III facility. There was considerable variation between the REAC data, generated off site, and the on-site data available from the facility. The differences in the meteorological conditions were believed attributable to local topographical features, which allowed channelling and eddy formation. The meteorological data generated at the facility was used to correlate the wind conditions and locations of the source of the plumes.

Summa canister samples were taken in several plumes so analyses for targeted and non-targeted compounds could be performed by conventional GC/MS methods. The canisters were also analyzed by the TAGA 6000E. The results of these analyses are located in Table II. The results between the two techniques showed good agreement for the target compounds, particularly when concentrations were elevated.

Conclusion

The goals of this investigation were successfully met. The TAGA 6000E identified off site plumes using target compounds; the sources of these plumes were located using meteorological data collected concurrently with the sampling; and the TAGA 6000E located plumes so whole-air samples could be collected in Summa canisters for target and non-target compounds analyses using conventional

GC/MS methodology. Furthermore, the Summa canister analysis for target compounds by both the GC/MS and the TAGA showed good agreement.

TABLE I. TARGET COMPOUND LIST

benzene*
chlorobenzene*
1,2-dichloroethane*
1,4-dioxane
methylene chloride*
1,1,1-trichloroethane
toluene*
xylene

* Identified from facility's Title III report.

TABLE II SUMMA CANISTER ANALYTICAL RESULTS (concentrations in ppb)

COMPOUND	SUMMA #41		SUMMA #69		SUMMA #67	
	GC/MS	TAGA	GC/MS	TAGA	GC/MS	TAGA
1,2-dichloroethane	ND	DL=4	ND	7J	ND	6J
benzene	QL=10	DL=6	95	74	QL=10	DL=6
methylene chloride	ND	DL=28	ND	DL=28	ND	30J
1,4-dioxane	ND	DL=6	ND	10J	ND	8J
toluene	QL=10	DL=13	18	22J	QL=10	DL=13
1,1,1-trichloroethane	QL=10	DL=4	QL=10	9J	39	42
xylene	QL=10	DL=8	QL=10	10J	QL=10	9J
chlorobenzene	ND	DL=2	9J	6	ND	DL=2

COMPOUND	SUMMA #52		SUMMA #1		SUMMA #48	
	GC/MS	TAGA	GC/MS	TAGA	GC/MS	TAGA
1,2-dichloroethane	ND	6J	ND	6J	ND	6J
benzene	QL=10	DL=6	117	139	235	229
methylene chloride	49	71J	QL=8	DL=28	QL=10	DL=28
1,4-dioxane	ND	8J	ND	DL=6	ND	8J
toluene	QL=10	DL=13	154	197	92	86
1,1,1-trichloroethane	ND	5J	QL=8	5J	QL=10	5J
xylene	QL=10	10J	ND	DL=8	QL=10	9J
chlorobenzene	ND	DL=2	13	17	27	19

COMPOUND	SUMMA #12			SUMMA #58		
	GC/MS	GC/MS (DUP)	TAGA	GC/MS	GC/MS (DUP)	TAGA
1,2-dichloroethane	ND	ND	6	ND	ND	6J
benzene	20	20	22	QL=10	QL=10	DL=6
methylene chloride	QL=10	QL=10	35J	QL=10	QL=10	32J
1,4-dioxane	ND	ND	8J	ND	ND	10J
toluene	18	17	26J	QL=10	QL=10	14J
1,1,1-trichloroethane	ND	ND	9J	QL=10	QL=10	10J
xylene	QL=10	QL=10	9J	QL=10	QL=10	10J
chlorobenzene	3J	ND	4J	ND	ND	DL=2

ND = Not detected

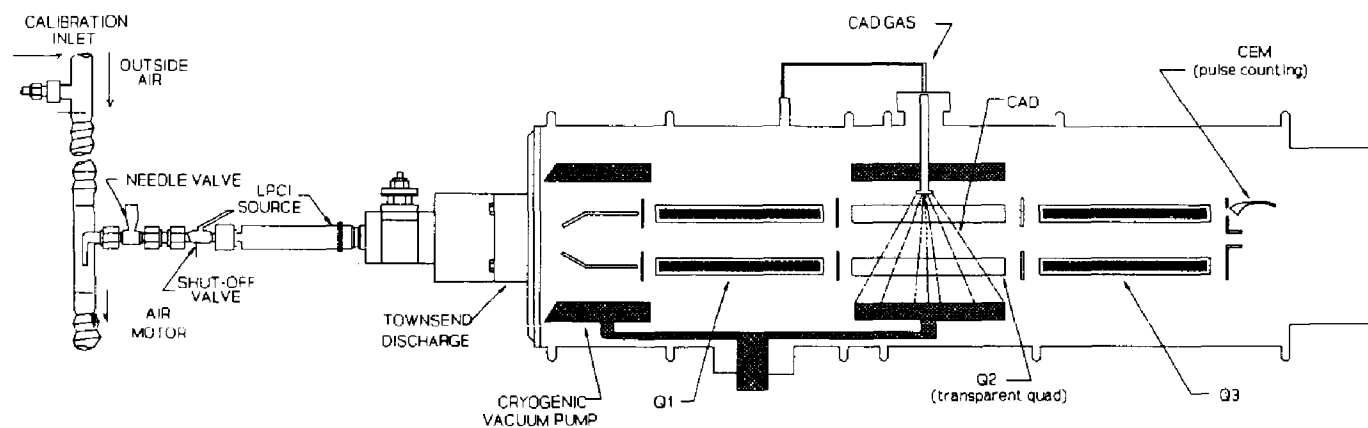
DL = Detection Limits

J = Value between Detection Limits and Quantitation Limits

QL = Quantitation limits

DUP = Duplicate

TAGA 6000E TANDEM TRIPLE QUADRUPOLE MASS SPECTROMETER



US EPA ENVIRONMENTAL RESPONSE TEAM
RESPONSE ENGINEERING AND ANALYTICAL CONTRACT

68-03-3482

Figure 1. The TAGA 6000E Mass Spectrometer.

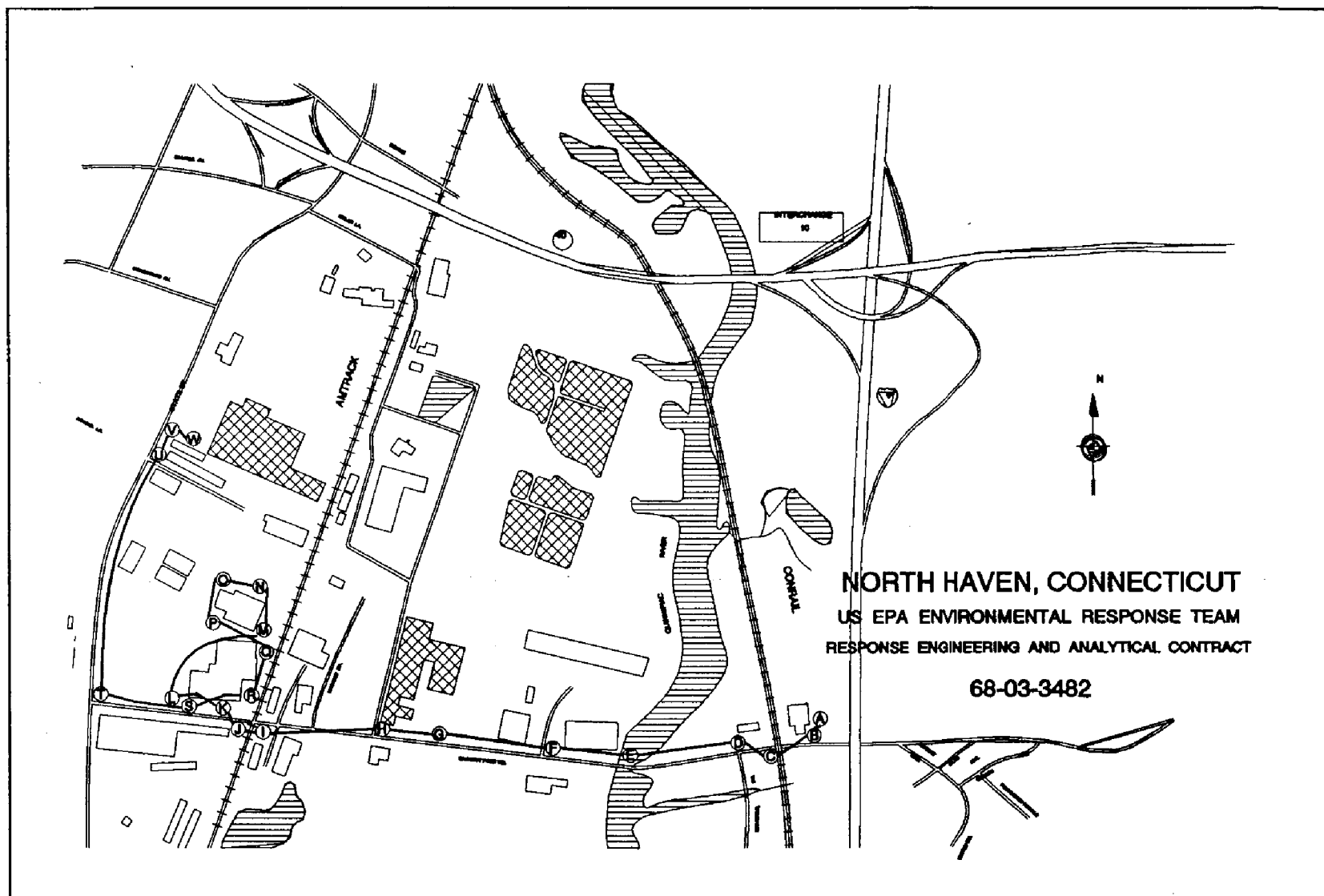


Figure 2. A Route Traversed To Perform Air Monitoring.

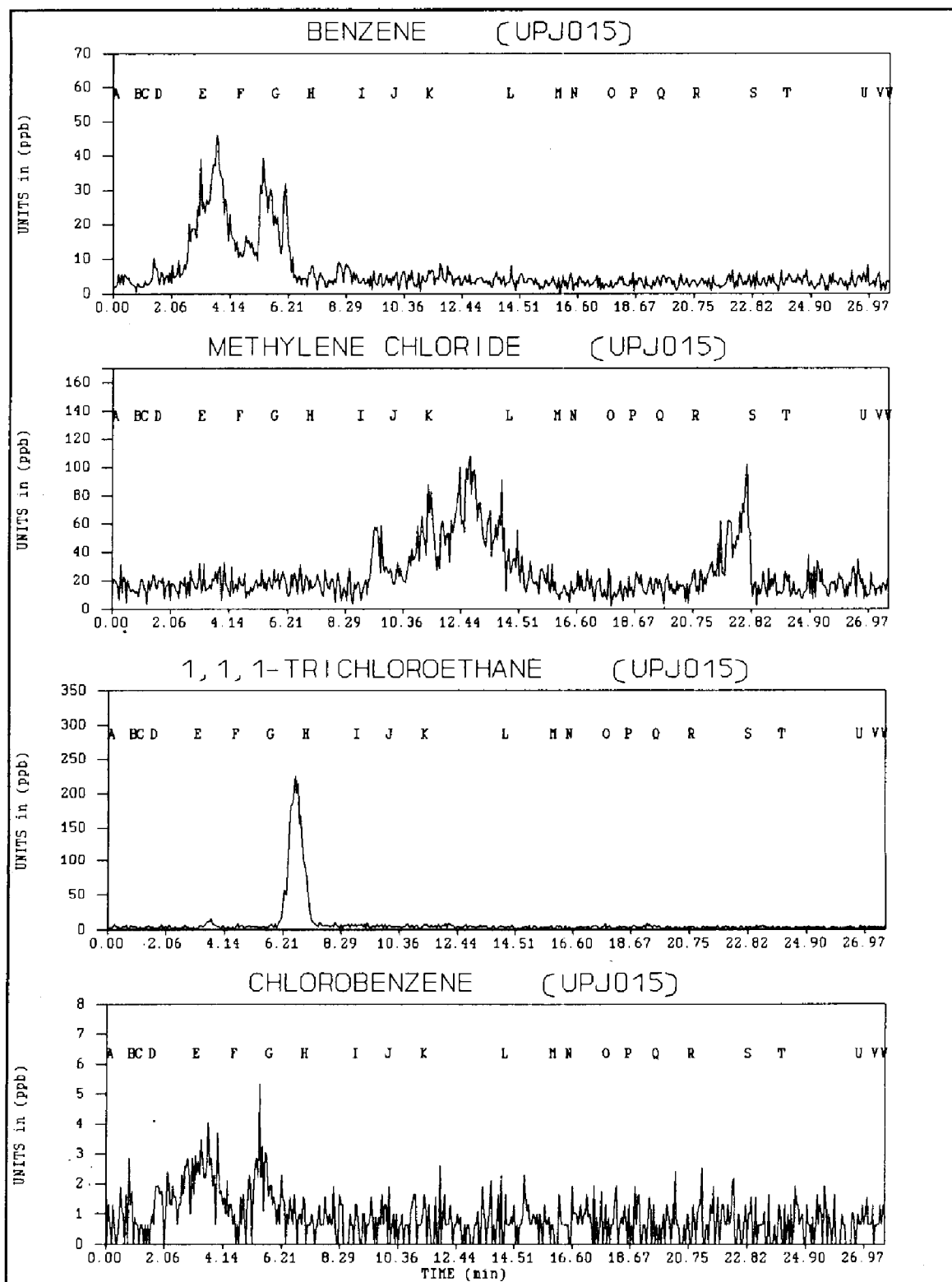


Figure 3. Ion Profiles For Target Compounds.

**DEVELOPMENT OF A "STATEMENT-OF-WORK (SOW)
FOR THE ANALYSIS OF AIR TOXICS AT SUPERFUND SITES"
AS PART OF THE CONTRACT LABORATORY PROGRAM (CLP)**

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ABSTRACT

As specified in the Comprehensive Environmental Response, Compensation and Liability Act of 1980 (CERCLA) and the Superfund Amendments and Reauthorization Act of 1986 (SARA), EPA has the responsibility for assessing the potential of air emissions and air quality impacts prior to and during Superfund hazardous waste site cleanup. CERCLA and SARA mandate the characterization of all contaminant migration pathways from waste to the environment and of the resulting environmental impacts. Specifically, they mandate that "all potential migration pathways for contaminants" be characterized. Heretofore, the U.S. Environmental Protection Agency (EPA) has developed specific Statement-of-Work (SOWs) to provide laboratories with specific analytical techniques in the analysis of both organic and inorganic analytes in soil, sediment and water as an integral part of the Contract Laboratory Program (CLP). In addressing the regulatory initiatives for assessing all pathways, the Analytical Operation Branch (AOB) of USEPA has initiated a project to develop a "Statement-of-Work (SOW) for the Analysis of Air Toxics at Superfund Sites" as part of the CLP. The objective of this paper is to outline the development of the SOW and briefly describe the analytical methodology for analysis of organics and inorganic air toxics.

INTRODUCTION

As specified in the Comprehensive Environmental Response, Compensation and Liability Act of 1980 (CERCLA) and the Superfund Amendments and Reauthorization Act of 1986 (SARA), the U.S. Environmental Protection Agency (EPA) has the responsibility for assessing the potential for air emissions and air quality impacts prior to and during Superfund hazardous waste site cleanup. CERCLA and SARA mandate the characterization of all contaminant migration pathways from waste to the environment and of the resulting environmental impacts. Both CERCLA and SARA regulations were developed within the Office of Emergency and Remedial Response (OERR).

Within the Hazardous Site Evaluation Division (HSED) of OERR is the Analytical Operation Branch (AOB), which administers the Contract Laboratory Program (CLP). The CLP provides analytical support service to Superfund and other EPA programs. The current SOWs address standardized analytical procedures for approximately 23 inorganic and 100 or more organic chemicals comprising the CLP hazardous substances list (HSL).

Within the CLP, the contract laboratory must adhere to defined methodologies associated with quality assurance/quality control (QA/QC), contract required detection limits (CRDL), reporting requirements and timeliness of data reporting as directed by the SOW. Present SOWs address organic and inorganic constituents in multi-media and at varying concentration levels. SOWs have been used in the CLP since its conception in 1980.

While the agency has numerous SOWs for soil and water, there was no guidance available for air toxics analysis of samples acquired during Superfund investigations. In order to provide technical support to EPA Regional Remedial Program Managers (RPMs) and Environmental Program Managers (EPMs) utilizing the CLP, AOB has developed a "Statement-of-Work for Analysis of Air Toxics at Superfund Sites" to be used as part of the CLP. This paper will outline its development in becoming a part of the CLP.

BACKGROUND

The development of the air toxics SOW involved several tasks. These tasks involved:

- Task 1 - Survey Involving Air Toxics Identification for Inclusion into a Target Compound List (TCL)
- Task 2 - Selection of Analytical Methodology Associated with TCL
- Task 3 - Preliminary "Statement-of-Work for Analysis of Air Toxics at Superfund Sites"
- Task 4 - Preliminary Multi-Lab Methods Validation for Primary Air Toxic Target Compound List
- Task 5 - Final Multi-Lab Methods Validation for Primary Air Toxic Target Compound List

- Task 6 - Final "Statement-of-Work for Analysis of Air Toxics at Superfund Sites"

To insure that Regional, state and commercial laboratory concerns were addressed AOB formed an Air Toxics Workgroup Committee (ATWC). The ATWC provided input and direction to the TCL (Task 1) and the selection of analytical methodology (Task 2) for those on the TCL.

The TCL consist of approximately 257 target compounds. Of the 257 compounds, 43% are volatiles thus having vapor pressure greater than 0.1 mm Hg. Within the volatile group, there are two basic sampling options: canister sampling and adsorbent methodology. A closer examination of the TCL illustrates that while most volatiles can be sampled by both canister and adsorbent, there are some volatiles which are amenable to one or the other methodology. Similarly, the detection limits are vary between the methods for specific volatiles on the TCL.

Approximately 32.4% of the TCL are classified as semi-volatiles with vapor pressures ranging from 10^{-1} to 10^{-6} mm Hg. Historically, the sampling methodology involves a filter combined with a combination polyurethane foam and XAD-2 plug to retain the semi-volatiles.

Metals comprise approximately 28% of the TCL. The sampling techniques normally involve filtration.

SELECTION OF ANALYTICAL METHODOLOGY AS PART OF THE AIR TOXICS SOW

The selection of the proper analysis method for an analyte is dependent on many important interrelated factors. These include the compound or compounds of interest, the level of detection required, the degree of selectivity needed, and the purpose of the data collected. Other factors which may be as important as the above are cost, the accuracy and precision required, and the number of samples to be sampled and analyzed.

In general, analytical methods selection were reviewed for inclusion into the Statement-of-Work from the following analytical publications:

- "Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air,"
- "Ambient Air Monitoring at Superfund Sites,"
- SW-846 entitled: "Test Methods for Evaluation of Solid Waste," and
- Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater.

Based upon the survey results, committee input and best available analytical techniques, the following analytical methodology, as outlined in Table 1.0, was selected to address groups of air toxics found on the TCL.

Table 1.0
SOW Analytical Methodology

<u>Classification</u>	<u>SOW Method</u>	<u>Sampling Technique</u>	<u>Sample Conditioning</u>	<u>Analysis Technique</u>
Volatiles	Method 1.1	Tenax [®] Adsorbent (Reference Method)	Thermal Desorption, Cryogenic Trapping and Focusing	GC/MS/SCAN
		Other Adsorbent (Equivalent Method)		
	Method 1.2	SUMMA [®] Canister	Nafion Dryer, Cryogenic Trapping (Reference Method)	GC/MS/SCAN
			Modified Water Purge, Adsorbent Trap, Then Thermal Desorption (Equivalent Method)	
Semi-volatiles, Including Pesticides and PCBs	Method 2.0	Filter Followed by PUF/XAD-2 Adsorbent Trap Using Hi- Volume Sampler	10% Ether/ hexane Soxhlet Extraction, Silica Gel Clean-up	GC/MS/SCAN
Metals	Method 3.0	Filter	Microwave Extraction Using HNO ₃ / HCl Acid Solution	ICAP

SOW ANALYTICAL METHODOLOGY DESCRIPTION

■ Method 1.1 - Volatile Organics Utilizing Solid Adsorbent

Conventional methods for VOC determination have relied on solid adsorbent techniques such as carbon and, more recently, Tenax[®]. For example, the U.S. Department of Health and Human Services, National Institute for Occupational Safety and Health base many of their sampling procedures on the use of carbon adsorption techniques. As with many solid adsorbents, there are many limitations to

the use of Tenax[®]. The more significant problems in utilizing Tenax[®] and other solid adsorbents are:

- Artifact formation,
- Contamination,
- Analyte breakthrough, and
- Solvent extraction

Although sorbent techniques demonstrate problems, several advantages can be gained through their use. First, integrated sampling over a period of 8 to 12 hours is easily performed. Because of the small size and portability of the sample tubes and pumps, they are easily located in many sampling application. Finally, multi-bed adsorbents can be used to sample different groups of volatiles, thus making their utility a major function of a monitoring protocol.

While there is reliable data to support a multibed tube, the reference method (RM) procedure utilizes Tenax[®] for the adsorptive media. This selection was based primarily on the years of experience the USEPA has on characterizing its weaknesses and strengths.

Sampling involves drawing ambient air through an adsorbent cartridge containing approximately 1-2 grams of Tenax[®]. While highly volatile organic compounds and most inorganic atmospheric constituents pass through the cartridge, certain organic compounds are trapped on the resin bed.

After the organics are trapped on the resin bed, the cartridge is tagged and transported back to the lab for analysis.

Upon receipt at the laboratory, the cartridge is logged into the lab book and the chain-of-custody form completed. The cartridges are stored under refrigeration until analysis.

As illustrated in Figure 1.0, the cartridge is submitted for analysis by GC/MS. During analysis, the cartridge is removed from the refrigerator, an internal standard is added to permit quantitative analysis, and the organics trapped on the Tenax[®] are thermally desorbed. The organic vapors are removed from the Tenax[®] by heating the sample cartridge to 275 C under a flow of helium. The desorbed vapors are collected in a cryogenic trap which is cooled to liquid nitrogen temperature. The use of the cryogenic trap allows the carrier gas flow, needed for the GC/MS, to be balanced.

The cryogenic trap containing the organics is then heated to transfer the sample to the head of the capillary GC column which is cooled to liquid nitrogen temperatures. This step is essential to focus the organic compounds and allow their application to the head of the capillary column in a discrete band.

The scan of the mass spectrometer is initiated and the analytical procedure is begun. Under a flow of helium, the GC column is programmed to a temperature to allow the elution of all of the organic compounds while the mass spectrometer is scanning. Data are recorded by the computer for subsequent processing. Quantitation is performed by the method of relative response factors, where the

proportionate system responses for analyte and standard are determined prior to the analysis of the sample and this relative system response is used to determine the quantity of compound present on the sample cartridge.

Component identification is normally accomplished, using a library search routine, on the basis of the GC retention time and mass spectral characteristics for a single ion for each target compound.

The quantitative analysis is performed by a combination of manual and computerized procedures: the computer is instructed to seek characteristic ions in a previously determined retention window. At this point the operator intervenes to determine if the compound of interest has been located correctly. If the compound identification is correct, the computer then performs the quantitative calculation using the method of relative response factors. Data are reported as ng/sample, and can be subsequently converted to whatever units are desired.

While the RM outlines the use of Tenax[®] as the adsorbent, the Statement-of-Work (SOW) will allow alternative adsorbent, i.e., multibed adsorbents, as equivalent methods. The Contract Laboratory must demonstrate accuracy and precision limits as well as sorbent characteristic data for selected analytes in order for other adsorbents to be classified as equivalent methods. In addition, the analysis of Performance Evaluation (PE) samples must meet the accuracy and precision limits. These limits are:

- Accuracy \pm 30%
- Replicate Precision \pm 30%

The accuracy and replicate precision limits were based upon data acquired over the last five (5) years from the Toxics Air Monitoring System (TAMS) utilizing the Tenax[®] solid adsorbent for monitoring volatile organic compounds.

■ Method 1.2 - Volatile Organics Utilizing Canister Methodology

Both subatmospheric pressure and pressurized sampling modes use an initially evacuated canister and a pump-ventilated sample line during sample collection. Pressurized sampling requires an additional pump to provide positive pressure to the sample canister. A sample of air is drawn through a sampling train comprised of components that regulate the rate and duration of sampling into a preevacuated SUMMA[®] passivated canister.

After the air sampled is collected, the canister valve is closed, an identification tag is attached to the canister, and the canister is transported to a predetermined laboratory for analysis.

Upon receipt at the laboratory, the canister tag data is recorded and the canister is attached to the analytical system. During analysis, water vapor is reduced in the gas stream by Nafion[®] dryer (if applicable), and the VOCs are then concentrated by collection in a cryogenically-cooled trap. The VOCs originally collected in the trap are revolatilized, separated on a GC column, then detected by one or more detectors for identification and quantitation.

The Reference Method (RM) involves using a micro-bore capillary column coupled to a mass spectrometer (MS) operated in the scan mode. The use of the GC-MS-SCAN detector system is recommended for positive identification and

quantitation of targeted compounds to assure that high-quality data is acquired. This configuration, as outlined in Figure 2.0 and Figure 3.0, will allow for the identification of target and non-target compounds. This methodology will be the reference method.

While the above procedure outlines the use of a Permapure[®] dryer to remove moisture prior to analysis by the GC/MS system, the SOW will allow alternatives to the Nafion[®] dryer/cryogenic trapping sample concentration step, if they can demonstrate meeting performance criteria by analysis of PE samples. Based upon historical data from the Urban Air Toxics Program (UATP) and Toxics Air Monitoring (TAM) monitoring systems operated by USEPA, the PE limits are:

- Accuracy: $\pm 30\%$
- Replicate Precision: $\pm 25\%$

These methods will be classified as equivalent methods. The SOW addresses the use of a modified purge-and-trap technique, as outlined in SW-846, Method 5030 entitled: "Organic Analysis-Purge-and-Trap Preparation and Extraction."

In one modification of the purge-and-trap technique (see Figure 4.0), the canister is evacuated to a large cryogenic trap at a rate of ~ 400 mL/min for a period of 10 minutes. The larger trap allows the analyst to acquire a larger sample for analysis to meet required detection limits. Once trapped, the gas stream is bubbled through a 1 mL water solution (to remove excess moisture) where the volatiles are efficiently removed from the aqueous phase to the vapor phase. The vapor is swept onto an sorbent column (analytical trap) where the volatile compounds are adsorbed. The analytical trap can be a combination of different sorbents (multi-bed trap). The analytical trap is backflushed for a short period of time (~ 2 minutes) to remove moisture. After purging is completed, the analytical trap is heated and flushed with inert gas to desorb the volatile organics onto the head of the GC column where they are cryofocused to improve peak shape and separation. After cryofocusing, the organics are separated on the GC column and identified and quantified by the MS.

Another modification to EPA methodology would allow the use of an analytical trap without the cryogenic trap, as illustrated in Figure 5.0.

The above modifications can all be used in the SOW as long as the analytical laboratory can meet Performance Specifications of precision and accuracy for PE samples. Figure 6.0 illustrates the various configurations allowed under the SOW equivalency program.

- Method 2 - Semi-volatile, Pesticides and PCB by Combination Filter/PUF/XAD-2 Adsorbent Cartridge

Semi-volatiles, pesticides and PCBs have received increased attention in recent years at Superfund sites because some of these compounds are highly carcinogenic or mutagenic. In particular, benzo[a]pyrene (B[a]P) has been identified as being highly carcinogenic. To evaluate the extent of human exposure to B[a]P and other semi-volatiles, reliable sampling and analytical methods are necessary.

Traditionally, a filter has been used to collect the semi-volatiles while polyurethane foam has been used to collect the pesticides and PCBs: Recent studies have indicated that during sampling non-volatile PAHs (vapor pressure

< 10^{-8} mm Hg), PCBs and pesticides may be trapped on the filter or adsorbent, but post-collection volatilization problems may distribute them downstream of the filter. To address this weakness, a combination filter followed by an adsorbent has been proposed as part of the Reference Method (RM).

A wide variety of adsorbents such as Tenax[®], XAD-2 and polyurethane foam (PUF) have been used to sample B[a]P and other PAH, pesticides and PCBs. All adsorbents have demonstrated high collection efficiency for B[a]P in particular. In general, XAD-2 resin has a higher collection efficiency for volatile PAHs than PUF, as well as a higher retention efficiency. However, PUF cartridges are easier to handle in the field and maintain better flow characteristics during sampling. Likewise, PUF has demonstrated its capability in sampling organochlorine pesticides, polychlorinated biphenyls and polychlorinated dibenzo-p-dioxins. However, PUF has demonstrated a lower recovery efficiency and storage capability for naphthalene and B[a]P, respectively, than XAD-2. There have been no significant losses of PAHs up to 30 days of storage at room temperature (23 C) using XAD-2. It also appears that XAD-2 resin has a higher collection efficiency for volatile PAHs than PUF, as well as a higher retention efficiency for both volatile and reactive PAHs. Consequently, while the literature cites weaknesses and strengths of using either XAD-2 or PUF, the RM recommends the sampling system to consist of a filter followed by a combination PUF/XAD-2 adsorbent. In order to reach needed detection limits, a high volume air sampler (10 cfm) has been recommended.

The analytical technique is a modification of EPA Test Method 610 and 625, Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater; Methods 8000, 8270, and 8310, Test Methods for Evaluation of Solid Waste; and Method 680, Determination of Pesticides and PCBs in Water and Soil/Sediment by Gas Chromatography/Mass Spectrometry. The choice of the gas chromatography coupled with mass spectroscopy was influenced by their sensitivity and selectivity, along with their ability to analyze complex samples.

Filters and adsorbent (PUF/XAD-2) cartridges are cleaned in solvents and vacuum dried. The filters and adsorbent cartridges are stored in screw-capped jars wrapped in aluminum foil (or otherwise protected from light) before careful installation on the sampler.

Approximately 360 m³ of air is drawn through the filter and combination adsorbent cartridge.

The amount of air sampled through the filter and adsorbent cartridge is recorded, and the filter and cartridge are placed in an appropriately labeled container and shipped along with blank filter and adsorbent cartridges to the analytical laboratory for analysis.

The filters and adsorbent cartridge are extracted by Soxhlet extraction using 10% ether/hexane. The extract is concentrated by Kuderna-Danish (K-D) evaporator, followed by silica gel cleanup using column chromatography to remove potential interferences prior to analysis by GC/MS, as illustrated in Figure 8.0.

The eluent is further concentrated by evaporation, then analyzed by GC-MS detection, as illustrated in Figure 7.0. The analytical system is verified to be operating properly and calibrated with five concentration calibration solutions using the internal standard approach. The mass spectrometer is operated in the SCAN mode so both target and tentatively identified compounds (TICs) can be addressed.

■ Method 3 - Metals

Particulate metals are defined as those elements that can be collected by standard filter media at ambient temperatures. Sampling methods for metal particulate are generally based on capture of the particulate on filter media. For the most part, glass fiber filters are used; however, organic and membrane filters such as cellulose ester and Teflon have also been used. The membrane filters demonstrate greater uniformity of pore size and, in many cases, lower background levels of trace metals than are found in glass fiber filters.

The basic particulate air sampler is the high volume sampler which collects a nominal m³ sample over a 24-hour period and captures particulate on an 8 x 10 inch filter (glass fiber). The nominal cut point is 100 μm for the maximum diameter particle size capture. A size-selective inlet can be placed ahead of the filter to separate respirable and nonrespirable particulate matter.

After collection, the filter can be stored in a manila folder and a protective envelope. The filter should be folded upon itself with the loading folded inside. Care should be taken so as not to damage or touch the filter and not to dislodge the loading.

The extraction procedure involves cutting a 1" x 8" strip from the Hi-Vol filter using a template as described in the Federal Reference Method entitled: "Determination of Lead in Suspended Particulate Matter Collected From Ambient Air." The strip is extracted by a microwave extraction procedure with a HNO₃/HCl acid solution for 23 minutes and analyzed by ICP, as illustrated in Figure 8.0.

The analytical system utilizes the inductively coupled argon plasma spectrometer (ICAP). ICAP enables multielement analysis (10-40 elements per minute) thus lending itself to the multielement requirements of the Contract Laboratory Program (CLP).

CONCLUSIONS

In response to CERCLA and SARA mandate programs to characterize potential air emissions and air quality impacts of air toxics through the air pathways, the USEPA/AOB has developed a SOW for the analysis of air toxics from Superfund sites to be used in the CLP. The SOW was developed through the guidance of the air toxics workgroup committee to insure that the needs of regional, state and local air pollution programs were addressed.

DISCLAIMER

Although the research described in this article has been funded wholly or in part by the United States Environmental Protection Agency through Contract 68-02-4398 to Engineering-Science, it has not been subjected to Agency review and therefore does not necessarily reflect the views of the Agency, and no official endorsement should be inferred. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

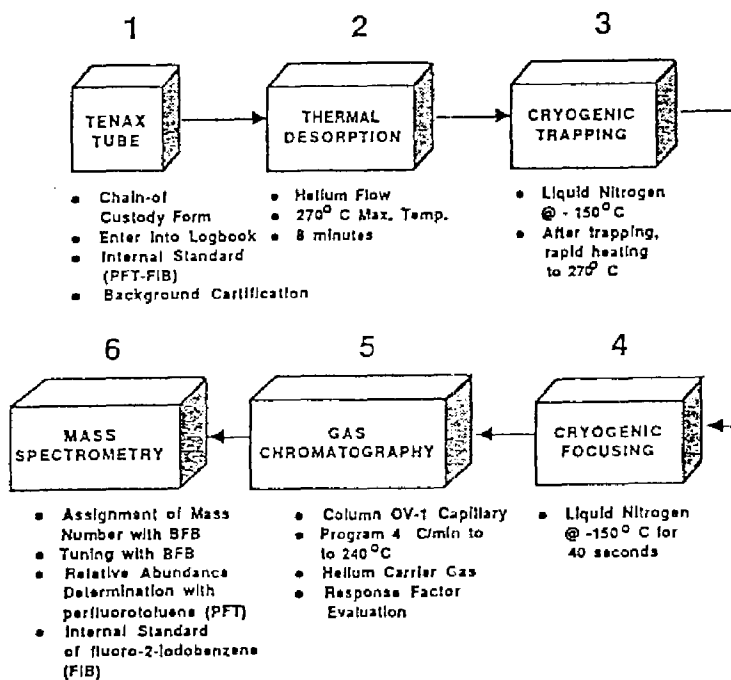


Figure 1.0. Strategy For Analyzing Volatile Organic Compounds Utilizing Gas Chromatography Coupled to A Mass Spectrometer from Tenax[®] Adsorbent Tubes.

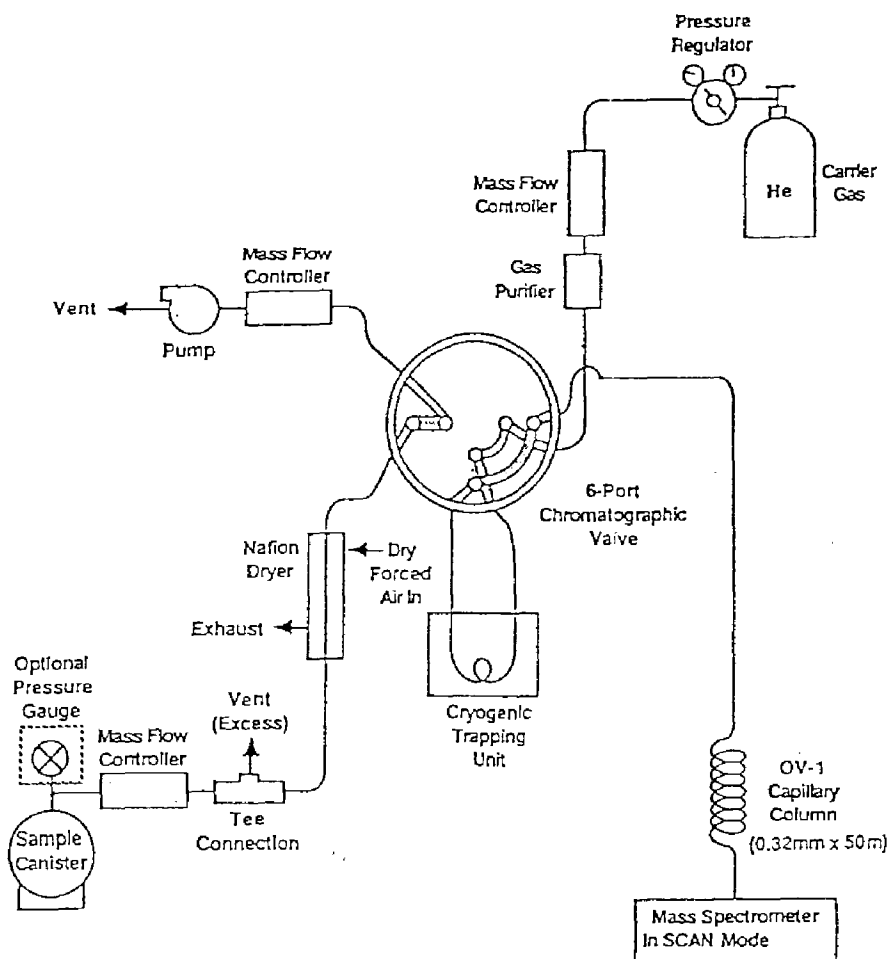


Figure 2.0. Strategy for Analyzing Volatile Organic Compounds Utilizing GC-MS-SCAN From SUMMA[®] Passivated Canisters As Reference Method 1.2.

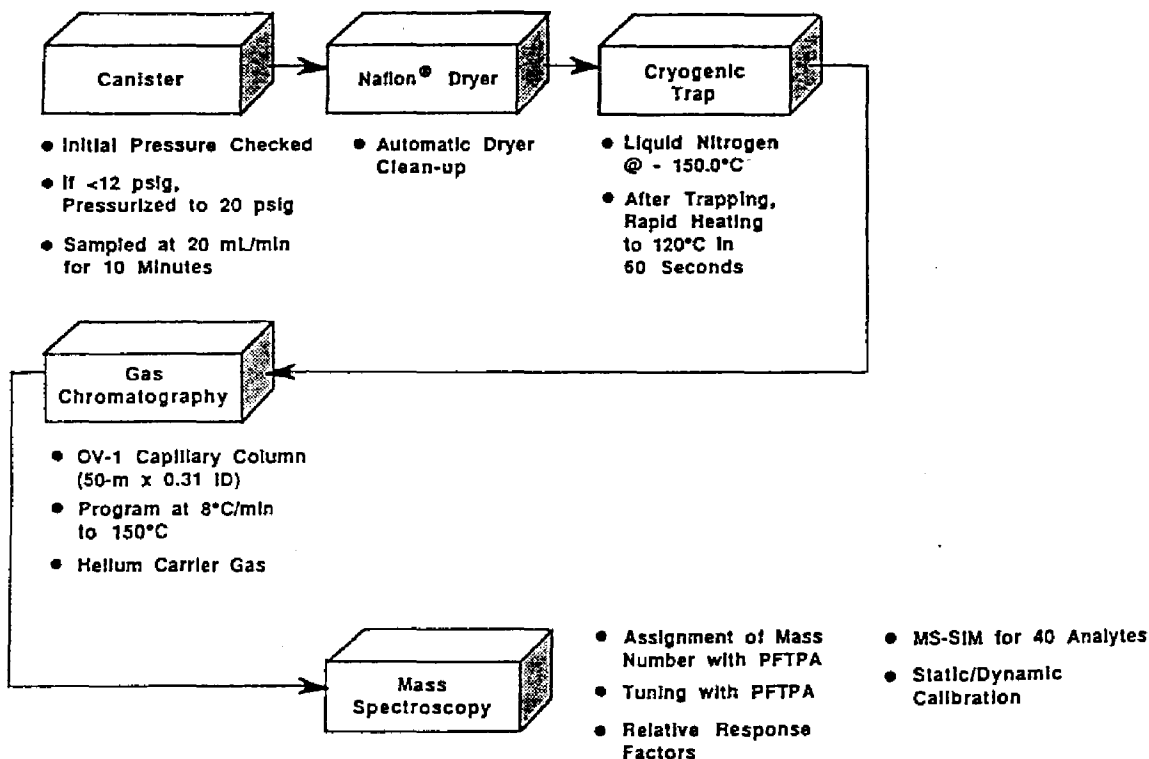


Figure 3.0. Reference Method 1.2 Analytical Method For Trace Organics In Gas Samples Collected By Canister.

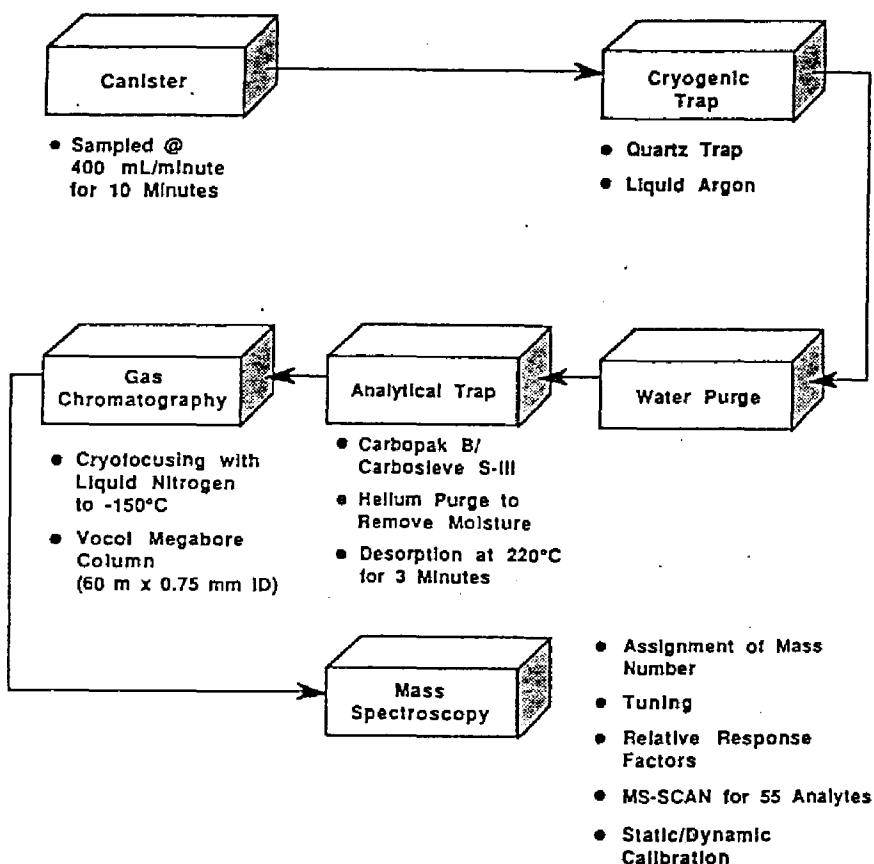


Figure 4.0. Equivalent Analytical Method For Trace Organics In Gas Samples Collected By Canister As A Modification To Reference Method 1.2.

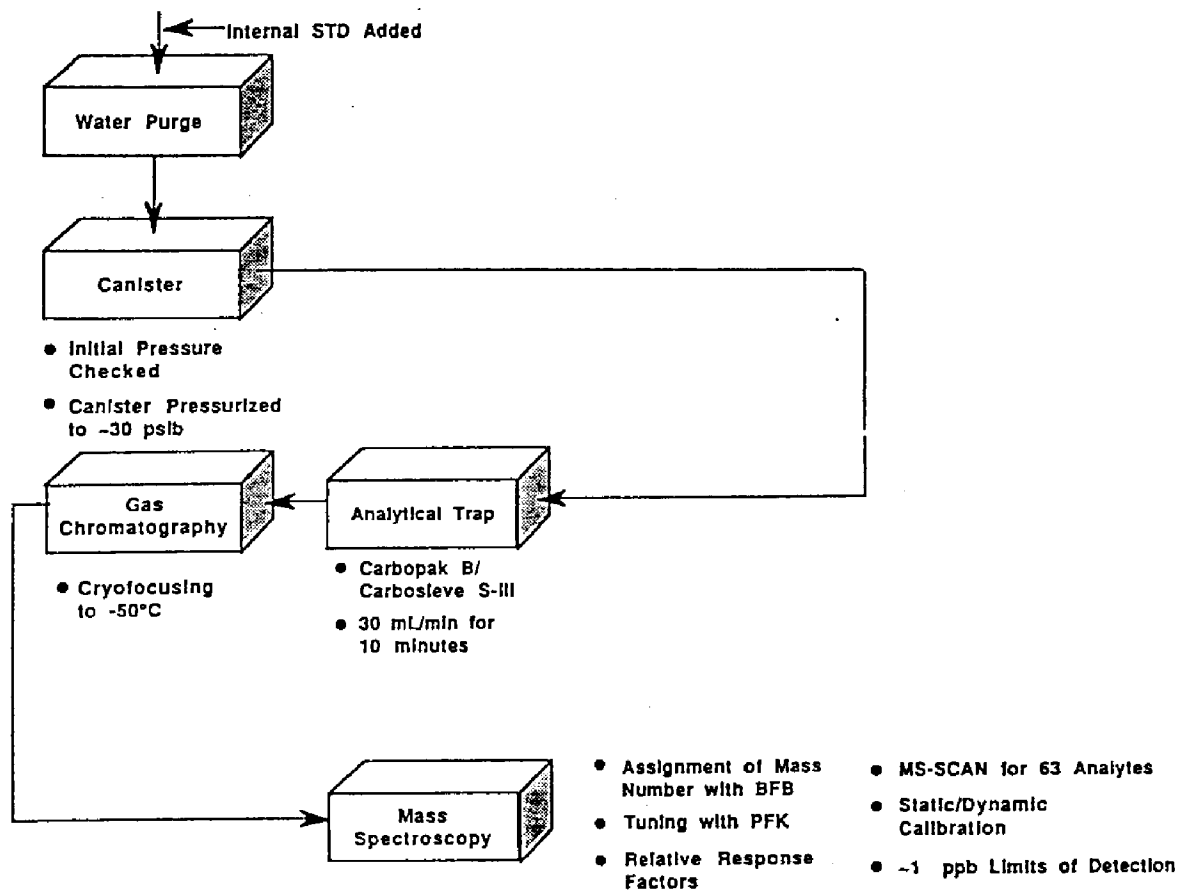


Figure 5.0. Equivalent Analytical Method For Trace Organics In Gas Samples Collected By Canister As An Alternative To Reference Method 1.2.

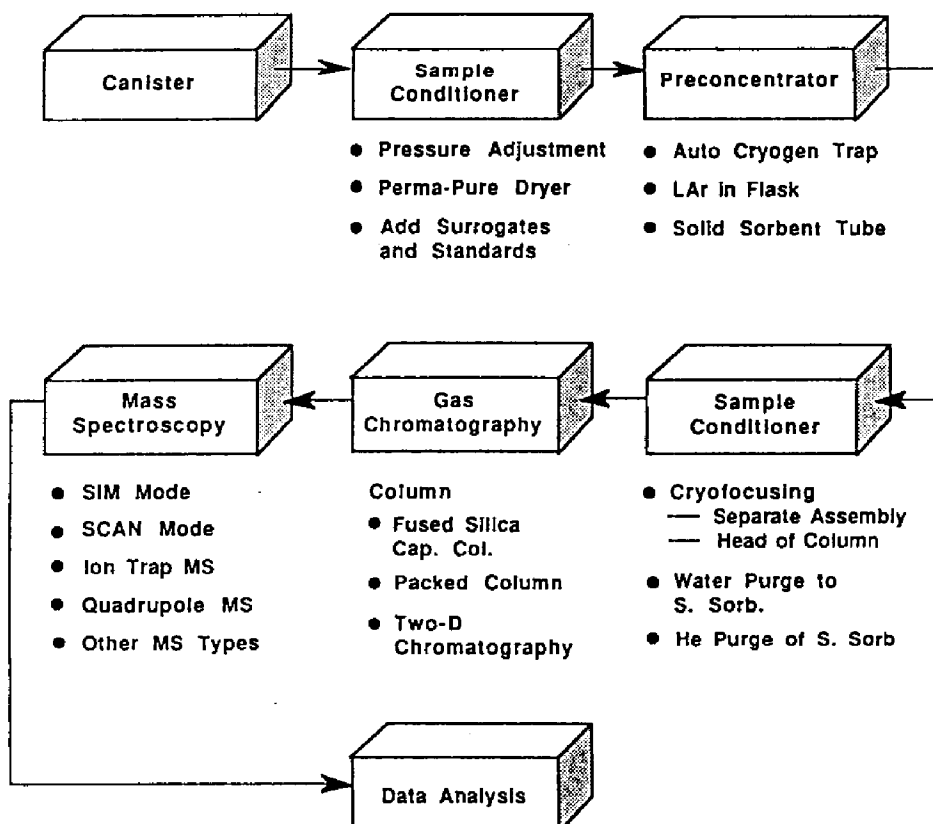


Figure 6.0. Generic Equivalent Analytical Method For Trace Organics In Gas Samples Collected By Canisters As An Alternative To Reference Method 1.2.

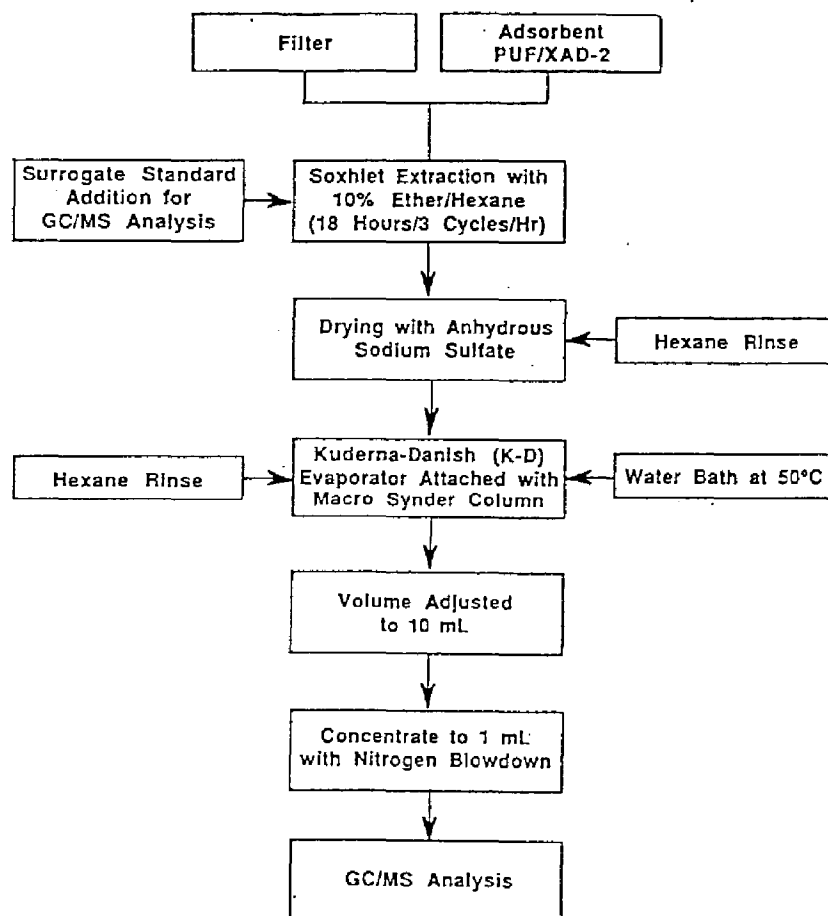


Figure 7.0. Strategy For Analyzing Semi-Volatiles and Pesticides Utilizing Combination Filter/Adsorbent (PUF/XAD-2 Combination) Followed By Gas Chromatography Separation With Mass Spectroscopy Identification.

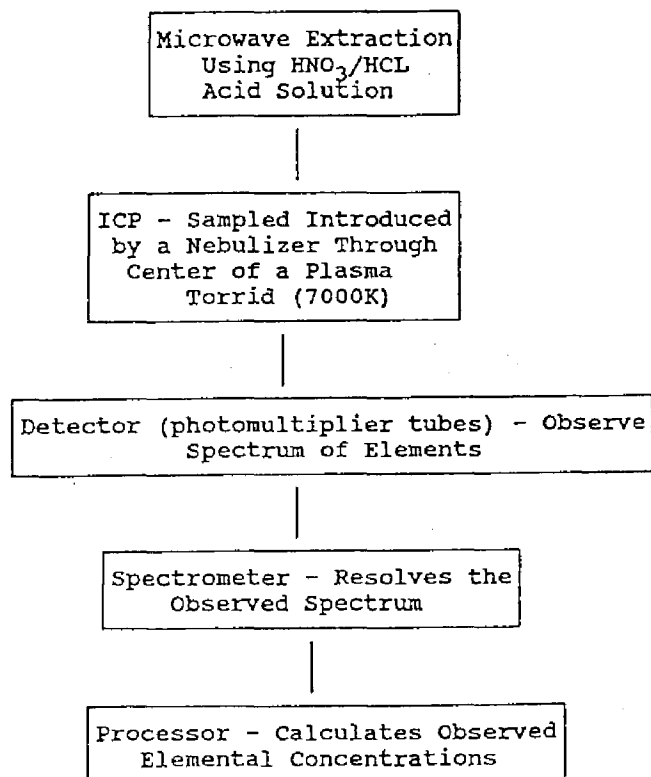


Figure 8.0. Strategy For Analyzing Metals On Glass Fiber Filters Utilizing Inductively Coupled Argon Plasma Emission Spectroscopy

**A PROGRAM TO VALIDATE AIR MONITORING METHODS
FOR THE SUPERFUND PROGRAM**

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EPA plans to accelerate its remediation and closure activities at Superfund sites and is committed to monitoring around these sites after closure to ensure that the remediation was successful. The increased activities at Superfund sites will increase the chances that toxic gases and contaminated soil particles (fugitive emissions) will be released to the atmosphere. Thus, it will be necessary to monitor the air over and around the sites using reliable methods to assure the site workers and the general population that they are not in any danger. Reliable methods will also be needed to ensure that the site remains harmless after closure. This paper describes EPA's efforts to validate its draft air monitoring methods for measuring the particle, semi-volatile organic, toxic metal and volatile organic concentrations over and around Superfund sites. The first phase of this effort will determine the precision and accuracy of the analytical portion of these methods through round robin testing. The experimental design, the types of samples, the analytes and the concentrations selected and the basis for their selection are described. The results obtained to date are also described.

INTRODUCTION

As Russ McAllister of our Office of Emergency and Remedial Response (OERR) discussed earlier today, EPA will establish a Contract Laboratory Program (CLP) for air samples collected over and around Superfund sites. In many ways this CLP program will resemble the current CLP program for soil and water samples. For example, each CLP laboratory must use an OERR-approved analytical method. Also, the analytical equipment and the analytes will be similar. There will be one significant difference, however. In the air sample CLP program the laboratory that will analyze the samples will provide the sample collection medium to the contractor who will collect the sample.

OERR is now developing four analytical methods for the air sample CLP program. OERR has a corresponding effort underway to develop air sampling methods compatible with these analytical methods. The four analytical methods and the material used to collect the air sample are:

- (1) VOC (volatile organic compounds) by Canister -- VOC's collected in a stainless steel 6-L canister, released into a cryogenically cooled cold trap for concentration and then quantitated by GC/MS;

(2) VOC by Tenax -- VOC collected on Tenax, thermally desorbed from the Tenax into a cryogenically cooled trap for concentration and then quantitated by GC/MS;

(3) Semi-VOC (semi-volatile organics) -- Semi-VOC collected by pulling air through a cartridge containing a filter, polyurethane foam and XAD-2. Semi-VOC's Soxhlet extracted, extract concentrated and semi-VOC's then quantitated by GC/MS. (Note: Semi-VOC's include pesticides and polychlorinated biphenyls.)

(4) Metals by Hi-Vol -- Metals collected on a quartz or glass-fiber filter, filter extracted with a microwave acid extraction and analyzed by ICP (preferred), FAA, AA or graphite furnace AA.

EPA's Atmospheric Research and Exposure Assessment Laboratory (AREAL) has agreed to validate the draft OERR analytical methods to establish for each analyte:

- (1) the precision and accuracy (bias) that can be expected under routine use by a qualified, experienced laboratory;
- (2) the clarity and applicability of the draft analytical method;
- (3) significant sources of error so that appropriate QC procedures can be included in the final draft of the method; and
- (4) target qualifying goals for OERR to use when selecting laboratories for the CLP program.

AREAL will: design the study; prepare, certify and distribute the samples; statistically analyze and reduce the data; and prepare a report on the results achieved. This paper describes how AREAL plans to conduct the validation study.

STUDY DESIGN

Six to ten laboratories will use the draft OERR analytical methods to analyze synthetic samples that closely simulate air samples that CLP laboratories will routinely analyze. Each laboratory will receive the same type and quantity of samples to analyze and report the results to AREAL using an AREAL-supplied form.

SELECTION OF PARTICIPANTS

Only laboratories that have the required analytical equipment on hand and have experience with the analytical method, or one very similar to it, will be considered. These restrictions are required for the validation study to provide estimates of the analytical method's performance in routine use. OERR's Sample Management Office (SMO) has already identified 15 to 20 qualified laboratories who are interested in participating. However, SMO cannot select the six to ten participating laboratories until the analytical methods become available later this month. Participants will be selected based on their competence, on their ability to analyze the samples in the 7 to 21 days specified and on the cost to OERR for them to participate.

SELECTION OF ANALYTES

The following approach was used to select the analytes. First, the OERR-ranked target compound list for the proposed CLP program was examined and the analytes OERR considered most important were identified. Then, an OERR data base that lists the number of times each proposed analyte was found in soil, water and waste samples from Superfund sites was examined. This was done to ensure that all analytes frequently encountered had been considered. (It is expected that the analytes in the soil, water and waste at a Superfund site will be the same as those that will likely be found in air samples from the site.) These two lists were compared to each other and to the inventory of available reference materials for the proposed analytes. The final list of analytes was then selected based on the above information and on AREAL's experience with the stability of the analytes in the sample collection medium (e.g., canister, Tenax, filter).

SAMPLE TYPES

As mentioned, samples that closely simulate an actual air sample will be used for each method. For the semi-VOC and metals methods, samples that represent a portion of the analytical method will also be used. These latter samples will provide OERR a rough estimate of the extraction efficiency of the analytical method. The number, type, and sample concentrations to be used are:

- (1) VOC-canister -- 6-L canisters (4 to 7) supplied by the participating laboratories will be spiked with up to 20 of the 36 candidate analytes. The concentrations will range from 1 to 40 ppb.
- (2) VOC-Tenax -- Tenax cartridges (4 to 7) supplied by the participating laboratories will be spiked with up to 20 of the 31 proposed analytes. Between 25 and 300 ng of each analyte will be placed on a cartridge.
- (3) Semi-VOC (pesticides) -- Three, filter/PUF/XAD-2 cartridges supplied by the participants will be spiked with up to 15 of the 21 proposed pesticide analytes. Each participant will also receive three solutions containing some of the same pesticides to evaluate the efficiency of their extraction. Cartridges will contain between 400 and 4000 ng and the solutions will contain between 400 and 4000 ng per mL.
- (4) Semi-VOC (non-pesticides) -- Same as for pesticides except the cartridges will contain between 50 and 350 μg and the solutions will contain between 10 and 100 μg per mL.
- (5) Metals -- Three solutions, three filters spiked with aqueous solutions of metals, and two soil samples will be supplied to each participant. Up to 14 of the 22 proposed analytes will be contained in the samples. The solutions will contain between 50 and 500 ng per mL; the filters will contain between 3 and 50 μg ; and the soils will contain between 50 and 200 μg per g.

REPORTING THE RESULTS TO AREAL

All participants will report their results using a form provided by AREAL. They will also report the source, the physical state, and the purity of all materials used to calibrate their analytical equipment.

STATISTICAL ANALYSIS OF THE DATA

For each method and analyte an analysis of variance (ANOVA) will be done^(1,2). This assumes that the variances are found to be homogeneous. Confidence limits for precision and accuracy will then be derived for the analyte. For each method, a multi-variant ANOVA will also be done for all analytes to obtain additional information on the performance of the method. A ranking approach such as that described by Youden⁽³⁾ may also be done, particularly if the variances are found not to be homogeneous.

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DISCLAIMER

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REDUCING UNCERTAINTIES IN INHALATION RISK ASSESSMENTS

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Assessment of inhalation risks at hazardous waste sites requires estimation of ambient air concentrations of toxic contaminants at locations near the site. This estimation may be developed through ambient air monitoring or emissions and dispersion modeling. Either approach may be uncertain by more than an order of magnitude. Uncertainties in ambient air measurements are related to difficulties in establishing the representativeness of the measurement time and location, particularly for sampling programs of short duration. Uncertainties in modeling approaches are dominated by difficulties in obtaining emissions information, but may also be affected by terrain features. Hybrid techniques in which the strengths of each approach are exploited may lead to a substantial reduction in the uncertainty of the final risk estimate. Application of these techniques require close collaboration between the modeling and measurement communities.

Introduction

Air pathway analyses (APA) are conducted at Superfund sites to evaluate inhalation exposures to the toxic chemicals found at the site. Both baseline risks and risks associated with remediation are generally assessed. A number of guidance documents are available to assist the analyst¹⁻⁵.

Air emissions mechanisms at hazardous waste sites include: volatilization through the soil cap of chemicals presently in soils, condensed phases, and ground water; release of chemicals from ground water to surface water with subsequent volatilization both at the ground water release point and at downstream locations; and resuspension of chemicals on soils and sediments.

Risk assessors must evaluate annual average and maximum short term (8- or 24-hour) inhalation exposures and risks attributable to each emitting area and for the site as a whole at nearby residences, work sites, and recreational areas. In many states, fence-line concentrations of toxic air contaminants (TACs) for various averaging times are needed for comparison with state reference values.

Each of these inhalation risk assessment activities requires the assessor to develop a representation of the atmospheric concentration field for each component attributable to each site of contamination. This field is combined with human activity factors to yield exposures, and with unit risk factors (where available) to yield risks. Uncertainties inherent in the unit risk factors are well known but not particularly interesting as long as the same factors are used in all risk assessments. These remarks will be addressed, therefore, to improving exposure estimates.

At present, inhalation exposures are generally assessed through either air quality modeling or monitoring. Interested parties frequently suggest that monitoring results, where available, are preferable to modeled results. However, this is seldom true. Monitoring data may yield point concentration estimates with remarkable accuracy, but establishing the spatial and temporal representativeness of these results is very difficult. On the other hand, modeling approaches are not reliable when emissions are not well known, where concentrations must be estimated at a particular site, or where complex terrain is an issue.

In practice, a combination of modeling and monitoring activities is needed to produce exposure estimates of acceptable certainty. This paper provides a description of the limitations of each approach alone and suggests several ways these activities can be integrated to produce exposure estimates of lower uncertainty than those produced by either method alone.

Limitations of Ambient Monitoring Data

The principle limitation of monitoring data is the question of representativeness. Ambient air measurement techniques are rapidly becoming very good so that point estimates for many contaminants can be obtained with uncertainties in the range of one to ten percent for many contaminants, even at very low concentrations. However, these point source estimates generally do not provide adequate measures of average and maximum exposures, even at the measurement point, unless a very extensive monitoring program is undertaken. Difficulties in obtaining representative data in short term sampling programs occur both because of meteorological variability and source strength variability in both time and space.

A simple thought experiment indicates that the minimum uncertainty in annual average ground level concentrations obtained through a one week sampling campaign at a typical hazardous waste site is likely to be on the order of six to eight. The corresponding maximum 24-hour concentration actually cannot be assessed with any certainty in such a campaign.

We have estimated, using the ISCST model, the average annual and short term ground level concentrations (GLCs) and GLC variability associated with unit emissions from two typical uniform ground level area sources having widths of 300 and 10 m respectively. In each case, the concentrations are assessed at a distance of 300 m from the source center using meteorological data from Tulsa, Oklahoma.

The projected maximum annual average concentration for the small source is about twice the estimated concentration for the large source (Figures 1a and 1b). The ratio of maximum daily average concentrations for the two sources is about 5 (Figures 1c and 1d). Weekly average concentrations (block averaged) differ from the average concentrations by a factors up to 4 for the large source and 8 (excluding two near-zero values) for the smaller source (Figures 1a and 1b). Examination of the frequency distributions of the weekly averages indicate that the 95% confidence limits GLCs for the two sources differ from the average by about the same factor (figs 1e and 1f). Thus, the measurement results have an minimum inherent uncertainty of a factor of at least 6-8 for the small source at any one location. In fact, for any randomly selected week, the probability is about equal for the small source that an average concentration will be obtained that is half the actual annual average GLC as that the actual annual average will be obtained.

The differences associated with source size arise because wind direction variability is more significant for the small source. The directional variability of the location of maximum concentration is uncertain by about a factor of two (not shown), so the overall minimum uncertainty in a measurement program intended to determine the maximum average off-site concentration for this type of source is about an order of magnitude.

For cases where emissions are not constant (e.g. fugitive dust) or not uniform, or where terrain complications are important, the overall uncertainty in the maximum average concentration will be considerably more than an order of magnitude.

Limitations in Modeling Approaches

Assessment of exposures via modeling requires estimating both an emissions term and a diffusion parameter in air.

Emission estimates

Emissions estimates for the various types of sources can be derived using methods described in several EPA guideline documents ^{1,4,5}. Emissions of fugitive dust from undisturbed soil and from transportation and earth-moving activities are well characterized. Emissions estimates can be obtained from the general equations (rated A) in Chapter 11 of AP-42, from data on limestone and other surface mines (given elsewhere in AP-42), or from rules of thumb given in the Superfund guidance documents. Unfortunately, the Superfund data sometimes yield emissions estimates that may be as much as several orders of magnitude lower than the AP-42 data.

Emissions from lagoons and other water bodies can be obtained with some assurance given detailed information on the nature and concentrations of the contaminants using existing information on the rate of loss of contaminants from water. However, for concentrated lagoons, loss rates may be reduced by contaminant complexation within the water. Models have not been developed to address either concentrated sludge or the issues of multi-layer lagoons having dilute water covers on sludge bottoms.

Emissions through the soil cap of volatile components in contaminated soils and groundwater through the soil cap may be computed using the Shen transport equation^{4,5}. This method assumes that each contaminant is transported vertically to the surface at a rate determined by its subsoil equilibrium vapor pressure, its diffusivity in air, the soil thickness, and the dry porosity of the soil. For many sites, especially in the baseline condition, through-soil volatilization yields the most signifi-

cant exposure estimates and drives the risk assessment. Unfortunately, it is also the area in which emissions calculations are least certain.

For this computation, the largest uncertainties are in the areas of soil moisture and soil porosity. Projected emissions for dry soil are about 2000 times those for soil in which 90% of the soil pores are filled with water. Packed soil and cement caps may reduce emissions, but they cannot be considered an absolute barrier. For instance, emissions will be released from under the concrete pad whenever the pad is broken for construction (and these emissions would contribute to the 70 year exposure). Continuous emissions should be anticipated from cracks and other imperfections in all of the hard covers. Uncertainties in the nature of the subsoil contaminant (and therefore, in subsoil vapor concentrations) may also be important. Through soil emissions are also sensitive to the hypothesized source size. Because total emissions are computed using average and maximal emissions rates per unit area and hypothesized emissions areas, uncertainties in total emissions for through soil emissions are proportional to the uncertainty in this parameter.

Atmospheric Transport and Dispersion

The availability of well characterized atmospheric transport models allows computation of annual average and maximum ground level concentrations with some assurance. However, the locations at which these maximal values occur and the maximal concentrations as a pre-determined point (such as a specific residence) are projected with much less certainty.

Difficulties in projecting GLCs occur when terrain issues intervene, and may be significant when emissions are released in ravines, from elevated lagoons, or in mountainous terrain.

Integrating Modeling and Measurement Activities

Major reductions in the uncertainty of risk assessments may be made by combining modeling and measurement efforts. Two major areas of opportunity exist: use of measurement techniques to improve emissions estimates and use of dispersion modeling for designing monitoring activities and interpreting the results.

Measurements that can be made to improve emissions estimates include studies of soil porosity and moisture, surface and subsoil contaminant states, soil absorption coefficients, and gross though soil emissions at well characterized locations. If these measurements are conducted with a particular modeling approach in mind, they can lead to a substantial improvement in emissions modeling results. However, measurements of soil emissions at point locations are not, by themselves, adequate unless their representativeness can be demonstrated through concurrent modeling or correlative measurement activities. Likewise, the usual soil gas surveys are of little use since they are a measure of static, not dynamic transport. However, measurements of soil vapor as a function of depth can be fitted with soil transport models to yield emissions estimates.

Ambient air measurements can also be designed to enhance transport modeling. Two considerations are necessary. First, the monitoring network should be established with the aid of modeling results similar to those in Figure 1 for the situation to be evaluated. These should be developed using the best possible representation of the emitting sources (including stack emissions points) and local meteorological data. This analysis provides information both on the best locations for samplers, and on the number of sampling units and length of record necessary to obtain data of adequate reliability. Second, the monitoring should be designed to feed information back to the model (so that short term maximum concentrations can be estimated). Examples of such designs include:

- o Measurements of GLCs and concurrent meteorological conditions adjacent to large lagoons or fugitive dust sources to obtain data that can be back-calculated using appropriate modeling tools to give area-averaged emissions rates. These measurements can be enhanced by the use of two

pairs of wind-controlled samplers that operate concurrently as upwind-downwind monitors (with time charts so the sampling period can be determined). These samples can be integrated over multiple days. Use of narrow wind acceptance criteria improves the usefulness of the data, but may lengthen the elapsed time needed to get an adequate sample.

- o Measurements using wind-controlled sampling devices to give information on ambient concentrations at specific locations for various specific meteorological conditions (shown by modeling to be diagnostic), the frequency of occurrence of which can be obtained from nearby meteorological records to obtain an estimate of annual averages.
- o Measurements, as a rough check on the models, of particular cases expected to give high concentrations. For instance, measurements of concentrations within a ravine under light nocturnal flow.
- o Measurements of TAC flux across a fenceline or other boundary obtained by suitably designed long-path length measuring devices. Again, the number and location of such devices should be determined with a particular modeling approach in mind.
- o Real time measurements of emissions from during preliminary site preparation activities using micro-balance or optical monitors to obtain data useful in projecting the risks of full remediation

Each of these designs should be developed to maximize the number of independent measures of the parameter to be tested within the cost restraints of the project. For instance, two days of wind-controlled sampling with two pairs of samplers could yield four to six meteorologically distinct conditions at the edges of a lagoon, each of which could be used to generate an independent estimate of the emission strength of the lagoon. In contrast, normal upwind-downwind 8-hour samples would yield, at best, two independent measures. Two 24-hour samples without direction control would probably yield no usable data because of the variability of wind conditions during each period.

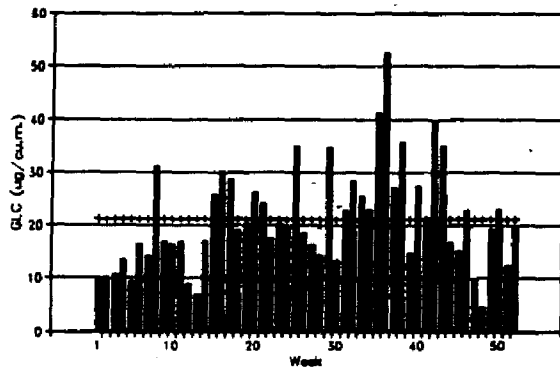
Conclusion

Both ambient monitoring and modeling approaches to risk assessment at hazardous waste sites may be uncertain by more than an order of magnitude. However, by combining the approaches in a thoughtful way, the strengths of each may be exploited to resolve the major areas of uncertainties in the individual approaches and produce a substantial reduction in the uncertainty associated with either approach alone.

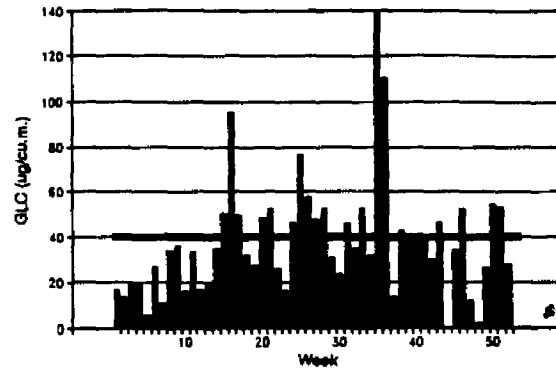
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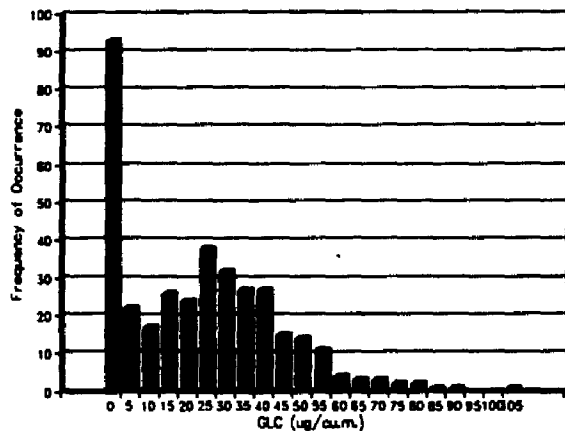
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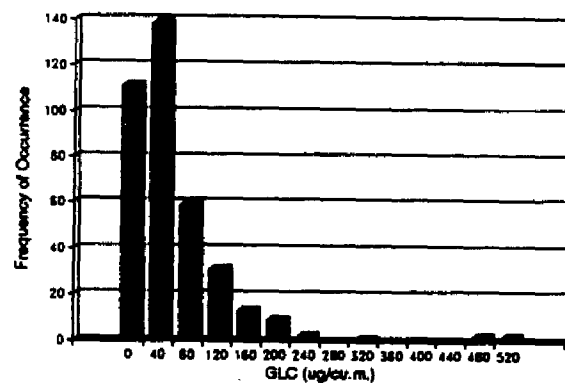
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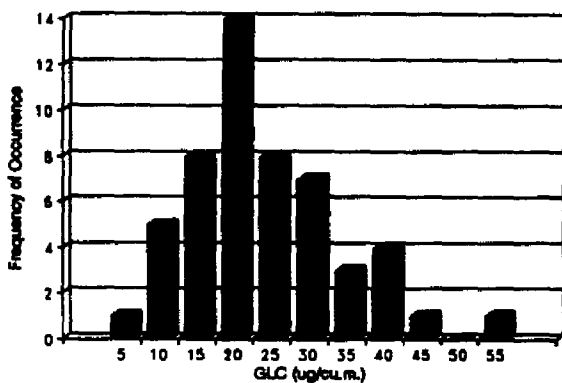
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d)



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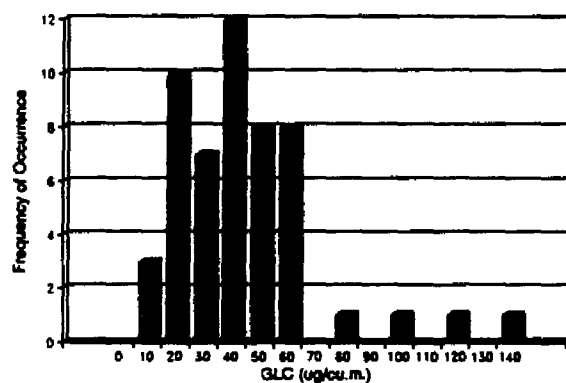


Figure 1. Summary statistics of atmospheric concentrations projected for unit emissions from uniform, ground level area sources: a) weekly block average GLCs and annual average concentrations for 300 m wide area source; b). Same as a, but for a 10 m wide source; c) and d), frequency of occurrence of daily average concentrations for the 300 m and 10 m sources, respectively; e) and f), frequency of occurrence of weekly average concentrations for the two sources.

DESIGN AND IMPLEMENTATION OF AN AIR MONITORING PROGRAM AT A SUPERFUND SITE

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A comprehensive air monitoring program was conducted during remediation activities at a Superfund site in New Jersey. The site was a chemical reclamation operation where chemicals such as hydraulic fluids, paints, varnishes, solvents, oils, plasticizers, and printing inks were processed between 1965 and 1979. By-products of processing operations were disposed of at the site and, as a result, the surface and subsurface soils were significantly contaminated with various organic and inorganic compounds.

An air monitoring program was designed to collect valid, representative measurements of compounds present in the air during remediation/clean-up activities. Air monitoring was conducted in the immediate vicinity of the site to protect the health and safety of site personnel and of the general public by ensuring that the ambient air quality was not significantly affected during remediation activities. During clean-up operations, air monitoring was conducted along the perimeter of the site using two sampling strategies. First, portable monitors for total volatile organic compounds and particulates were used to conduct real-time air measurements. Subsequent analysis of whole air samples was conducted using field gas chromatography/photoionization detection (GC/PID). These measurements provided real-time indications of off-site migration of the various target compound groups during remediation activities. Second, in order to validate the real-time data and provide more detailed documentation of site emissions, time-weighted average sampling methods using filter collection and/or solid sorbents were employed in the field. Samples collected were subsequently analyzed at specialized analytical laboratories.

The presented paper provides a discussion of the design of the air monitoring program, the collection of air quality data, and the interaction between air monitoring activities and remediation activities. The air monitoring program conducted at the site proved to be effective in controlling emissions. The ambient air quality was not significantly affected during the remediation, and as a result, the health and safety of both on-site personnel and the general public were protected.

Introduction

Under the direction of the United States Environmental Protection Agency (U. S. EPA) Region II, a Consent Order was issued to conduct remedial construction work at a former chemical reclamation facility located in southeast New Jersey. Operations at the facility included buying, selling, and processing chemical products such as hydraulic fluids, paints, varnishes, solvents, oils, plasticizers, and printing inks. By-products of these materials were disposed of on-site, and as a result, surface and subsurface soils were contaminated with various organic and inorganic chemicals. The abandoned reclamation facility consisted of a concrete block building, a distillation house, primary and secondary lagoons, a septic system, a tank farm, and an underground storage tank. The numerous remediation activities, including the demolition of existing buildings, the cleanup and removal of storage tanks, and the excavation of on-site and off-site soils, created the potential for off-site release of volatile organic compounds (VOCs), particulate matter, and trace elements.

The purpose of the air monitoring program was to design and implement an air monitoring strategy to control off-site emissions resulting from remedial activities, as well as to protect the health and safety of site personnel and the general public. Both real-time emissions measurements and time-weighted average (TWA) sampling were conducted to meet the objectives of the air monitoring program. This paper presents a discussion of the air monitoring design and strategy for selection of target parameters, selection of air sampling techniques, selection of sampling locations, and determination of corrective action measures for the subject site.

Design Strategy and Implementation

Selection of Target Parameters

A number of compounds, including VOCs, semi-volatile organic compounds (SVOCs), polychlorinated biphenyls (PCBs), lead, and chromium, were detected in samples collected at the site from numerous soil borings during previous site investigations. A modified risk assessment was conducted to select target compounds that would be monitored at the site. Specific target compounds were selected based on the following criteria:

- Concentration in the soil
- Frequency of detection in soil samples
- Toxicity
- Exposure limits
- Volatility

A ranking system was developed to make the final selection of target compounds.

Selection of Sampling Techniques

Based on the selection of target parameters and compounds, both real-time and TWA air sampling techniques were used to monitor air at the perimeter of the site. Instantaneous (real-time) field measurements for total VOCs were performed using an HNu Model PI-101 photoionization detector (PID). A real-time aerosol monitor, the GCA MINIRAM, was used

to measure real-time particulates. The MINIRAM is a portable, battery-operated instrument that measures airborne particulates. The instrument has a detection limit of approximately 0.01 mg/m³. A field gas chromatograph (GC) equipped with a PID was also used to identify real-time target compounds during the remediation activities. The GC/PID was calibrated daily. Samples for on-site GC/PID analysis were collected in gas-tight glass syringes and immediately analyzed.

Real-time monitoring program activities are summarized in Table I. The table lists the real-time parameters monitored for each of the 12 remediation activities. As shown in this table, the appropriate real-time monitoring was selected based on the nature of each specific remediation activity.

In order to validate the real-time data and to provide more detailed documentation of emissions from the site, manual, TWA sampling methods using filter collection and/or solid sorbents were conducted in the field, and subsequent laboratory analysis of the samples was performed. The sampling methods included TWA volatile sampling with Tenax adsorbents; total suspended particulates (TSP), lead, and total chromium sampling with Hi-Vol filters; and semi-volatile sampling for polychlorinated biphenyls (PCBs), naphthalene, and phenol with polyurethane foam (PUF)/XAD-2 sorbent cartridges. TWA volatile organic were collected, using a personal sampling pump, on a Tenax sorbent cartridge followed in series by a Tenax/charcoal cartridge.

TWA sampling program activities are summarized in Table II. The table lists the TWA sampling conducted for each of the 12 remediation activities. As with the real-time monitoring, the selection of appropriate TWA monitoring was based on the nature of each specific remediation activity.

Selection of Sampling Stations

Real-time monitoring stations were selected each day based on National Weather Service local wind forecast, prevailing wind direction recorded on-site by the meteorological monitoring station, and locations of on-site remediation activities. Real-time measurements for total VOCs using the HNu were conducted hourly at one upwind location and three to four downwind locations, as necessary, to determine total VOCs representative of conditions downwind of site activities. Additional locations were selected if needed. Real-time monitoring for particulates was conducted at the same times and locations as the VOC measurements using a MINIRAM monitor. More frequent monitoring (30-minute intervals) was performed when action level exceedances were encountered.

Locations for TWA samples were selected based on the criteria used to determine real-time monitoring locations. TWA samples, including specific VOCs, PCBs, naphthalene, phenol, TSP, lead, and total chromium were collected each working day. The required samplers were established at the selected locations and allowed to collect samples for approximately 8 hours.

Determination of Corrective Action Measures

Action levels were established for the real-time monitoring program based on negotiations with the U. S. EPA. Real-time measurements provided instantaneous indications of off-site

migration of various target compounds during remediation activities. Figures 1 through 4 summarize action levels and the required responsive steps.

If the HNu reading was 1 ppm or greater above the background level (upwind concentration), the on-site safety officer and project manager/field coordinator were immediately notified. In such cases, the frequency of monitoring was increased to 30 minute intervals, and downwind grab samples were analyzed using the Photovac GC/PID. The intervals between measurements remained at 30 minutes until the difference between the upwind and downwind measurements was less than 1.0 ppm for three consecutive 30-minute readings.

When the VOC levels at any downwind site exceeded those measured at the upwind site by 2.5 ppm or greater, the GC/PID was used to evaluate which real-time VOCs were present. The site coordinator was notified of HNu readings that remained at 2.5 ppm above background for 10 minutes so that a course of action could be chosen to bring the level of emissions below action limits. Possible courses of action included the use of vapor suppressant foams, work slowdown, and if necessary, work shutdown.

If the real-time particulate level at any downwind site exceeded that measured at the upwind site by 1.0 mg/m³ or more, the project manager was notified so further action could be taken to reduce emissions. No such action was necessary during the air monitoring program.

Criteria for Sample Analysis

TWA samples with the highest potential to provide useful, defensible, and representative data of the highest quality were prioritized each day for analysis. Samples were validated individually upon collection for analysis based on the following criteria:

- Meteorology
- Sampler operation
- Physical integrity of sample
- Proper sample documentation
- Field observations
- Exceedance of action levels

Although daily sampling was conducted to provide data for the thorough coverage of all potential emissions events, the above criteria were used to assure a cost-effective air monitoring program.

Results

The results of the real-time measurements for VOCs are shown in graph form in Figure 5. As shown, for the majority of the days measurements were taken, VOC concentrations were below 1 ppm.

The results of the GC/PID analyses also indicated that, for the majority of days monitored, no concentrations of VOCs above detection limits were identified. On days when one or more compounds were detected, for the majority of the day, VOC concentrations for all real-time target compounds were below detection limits. The compounds most frequently

detected by GC/PID were trichloroethene, toluene, and tetrachloroethene. These results are consistent with the results of the TWA sampling for VOCs. Concentrations of TWA VOCs recorded for an 8-hour average were, as expected, much lower than the instantaneous grab samples taken for on-site GC/PID analysis.

Several compounds were detected during the TWA sampling program. VOCs were also detected at the upwind sites at background levels. All downwind concentrations were below 130 ppb. The majority of concentrations were below 10 ppb.

The results of the real-time particulate measurements indicated that the highest instantaneous particulate concentration encountered was 0.4 mg/m^3 . Readings were therefore lower than the 0.5 mg/m^3 action level for the entire project. The majority of all readings were at or near background levels for the duration of the project. These results are consistent with the TWA TSP results. The highest concentration of TSP detected was $258 \text{ } \mu\text{g/m}^3$. The highest concentration of lead detected was $0.26 \text{ } \mu\text{g/m}^3$, and of chromium $0.02 \text{ } \mu\text{g/m}^3$. TSP levels for the majority of samples were below $100 \text{ } \mu\text{g/m}^3$, lead was below $0.1 \text{ } \mu\text{g/m}^3$, and total chromium was below detection limits.

The results of the analyses of TWA samples for PCBs indicated that only low levels of PCBs ($< 15 \text{ ng/m}^3$) were detected in the course of monitoring conducted during any of the site activities. Two other SVOCs (naphthalene and phenol) were collected on the same cartridge as PCBs. The results of the analyses for these compounds indicated only low levels of these compounds. The highest detected concentration of phenol was 0.19 ng/m^3 , and of naphthalene, 21.8 ng/m^3 .

Conclusions

The air monitoring program conducted at the Superfund site proved to be effective in controlling site emissions. The real-time monitoring program enabled the continuous and timely generation of data that provided useful emissions information during daily site remediation activities. This information allowed the field site coordinator and site safety officer to determine when appropriate corrective measures were required to reduce site emissions.

Because of the conservative nature of the real-time monitoring action levels, off-site impacts were minimized. The use of the GC/PID supported the HNu readings by identifying and quantifying the real-time target VOCs of concern at the site. The manual TWA monitoring program provided detailed information regarding the magnitude of emissions over 8-hour periods throughout the project. The data produced from the manual TWA monitoring correlated well with the real-time data. Analysis of Tenax, PUF/XAD-2, and Hi-Vol samples indicated that only low to average emission levels were detected at any time during the project.

The air monitoring program conducted at the site successfully accomplished its intended goals. The program demonstrated that the ambient air quality was not significantly affected during remediation activities and, as a result, the health and safety of both on-site personnel and the general public were protected.

TABLE I**Real-Time Monitoring Program**

<u>Site Remediation Activity</u>	<u>Monitoring Conducted</u>
1) On-Site Soils	Total VOCs (HNU PID), Real-Time Particulates (MINIRAM), Target VOCs (Photovac 10S GC/PID)
2) Off-Site Soils	Total VOCs (HNU PID), Real-Time Particulates (MINIRAM), Target VOCs (Photovac 10S GC/PID)
3) Concrete Block Building	Real-Time Particulates (MINIRAM)
4) Distillation House	Real-Time Particulates (MINIRAM)
5) Interior Process Tanks and Vessels	Total VOCs (HNU PID), Target VOCs (Photovac 10S GC/PID)
6) Exterior Process Tanks and Vessels	Total VOCs (HNU, PID), Real-Time Particulates (MINIRAM), Target VOCs (Photovac 10S GC/PID)
7) Underground Tanks	Total VOCs (HNU PID), Real-Time Particulates (MINIRAM), Target VOCs (Photovac 10S GC/PID)
8) Tank Farm	Total VOCs (HNU PID), Real-Time Particulates (MINIRAM), Target VOCs (Photovac 10S GC/PID)
9) Septic System	Real-Time Particulates (MINIRAM)
10) Excavation Area	Total VOCs (HNU PID), Real-Time Particulates (MINIRAM), Target VOCs (Photovac 10S GC/PID)
11) Secondary Lagoon Area	Total VOCs (HNU PID), Real-Time Particulates (MINIRAM), Target VOCs (Photovac 10S GC/PID)
12) Buried Waste Area	Total VOCs (HNU PID), Real-Time Particulates (MINIRAM), Target VOCs (Photovac 10S GC/PID)

TABLE II**Time-Averaged Sampling Program**

<u>Site Remediation Activity</u>	<u>Monitoring Conducted</u>
1) On-Site Soils	Target Volatiles (Tenax) PCBs, Phenols, Naphthalene (PUF/XAD) Particulates, Metals (Hi-Vol)
2) Off-Site Soils	Target Volatiles (Tenax) PCBs, Phenols, Naphthalene (PUF/XAD) Particulates, Metals (Hi-Vol)
3) Concrete Block Building	Particulates (Hi-Vol)
4) Distillation House	Particulates (Hi-Vol)
5) Interior Process Tanks and Vessels	Target Volatiles (Tenax)
6) Exterior Process Tanks and Vessels	Target Volatiles (Tenax) Particulates, Metals (Hi-Vol)
7) Underground Tanks	Target Volatiles (Tenax) Particulates, Metals (Hi-Vol)
8) Tank Farm	Target Volatiles (Tenax) Particulates, Metals (Hi-Vol)
9) Septic System	Particulates (Hi-Vol)
10) Excavation Area	Target Volatiles (Tenax) PCBs, Phenols, Naphthalene (PUF/XAD) Particulates, Metals (Hi-Vol)
11) Secondary Lagoon Area	Target Volatiles (Tenax) PCBs, Phenols, Naphthalene (PUF/XAD) Particulates, Metals (Hi-Vol)
12) Buried Waste Area	Target Volatiles (Tenax) PCBs, Phenols, Naphthalene (PUF/XAD) Particulates, Metals (Hi-Vol)

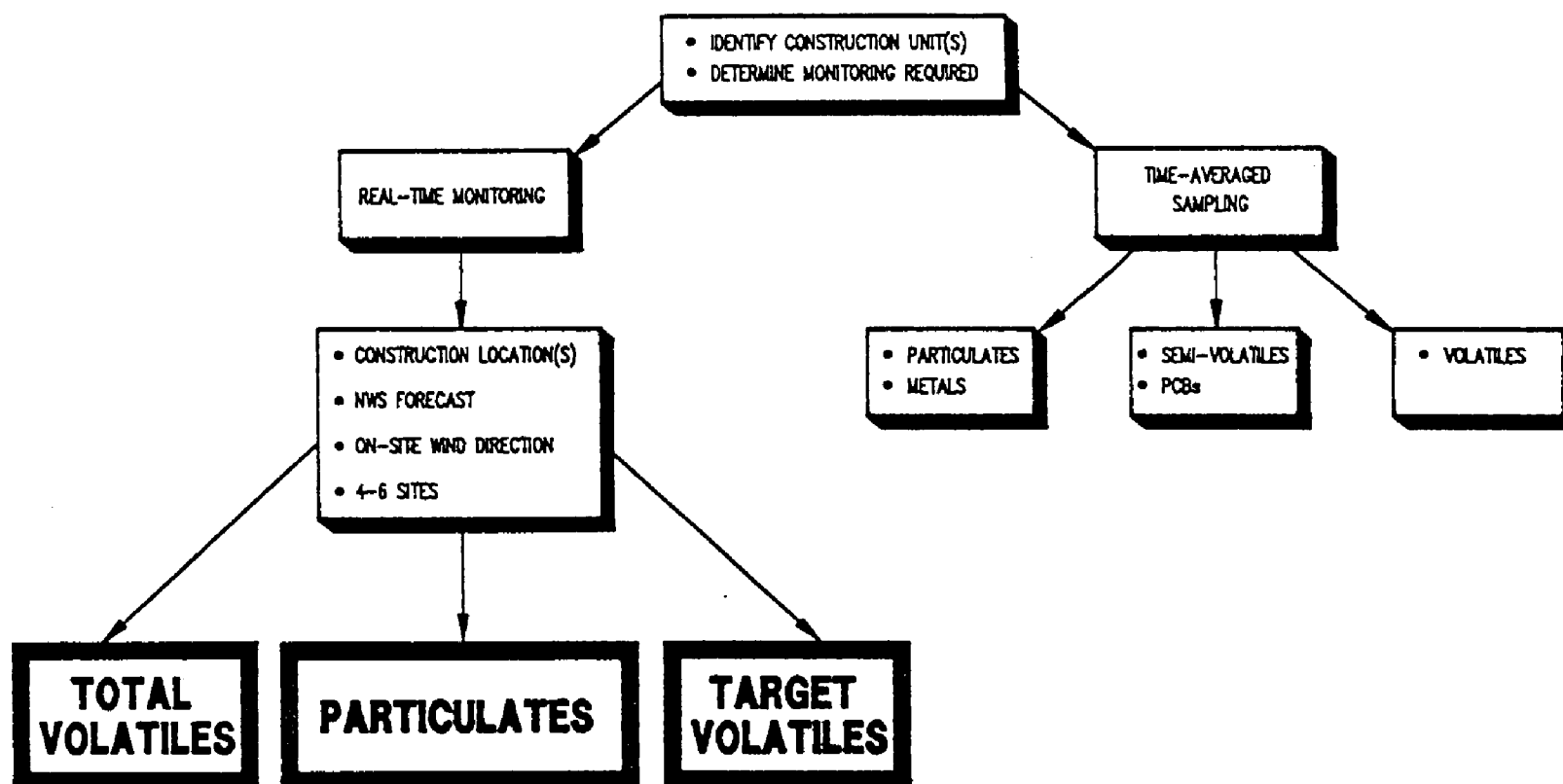


Figure 1. Air Monitoring Plan: Overview

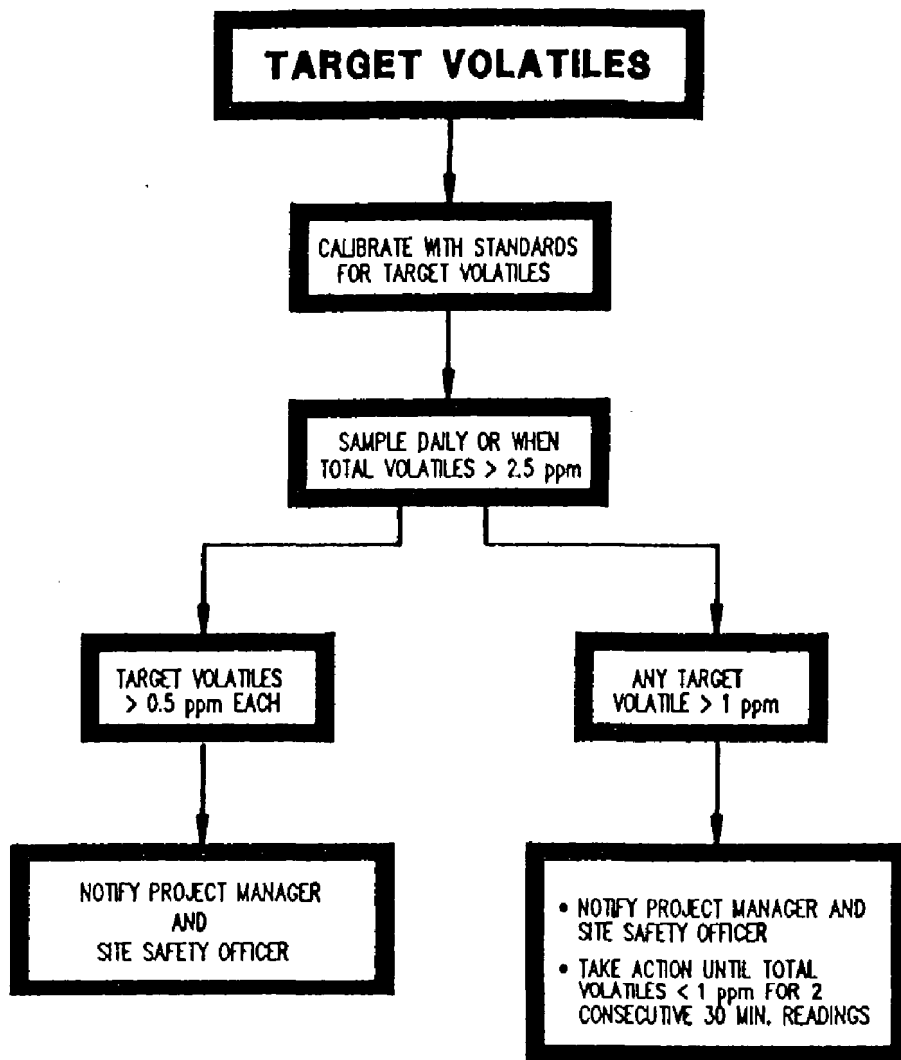


Figure 2. Air Monitoring Plan: Target Volatiles

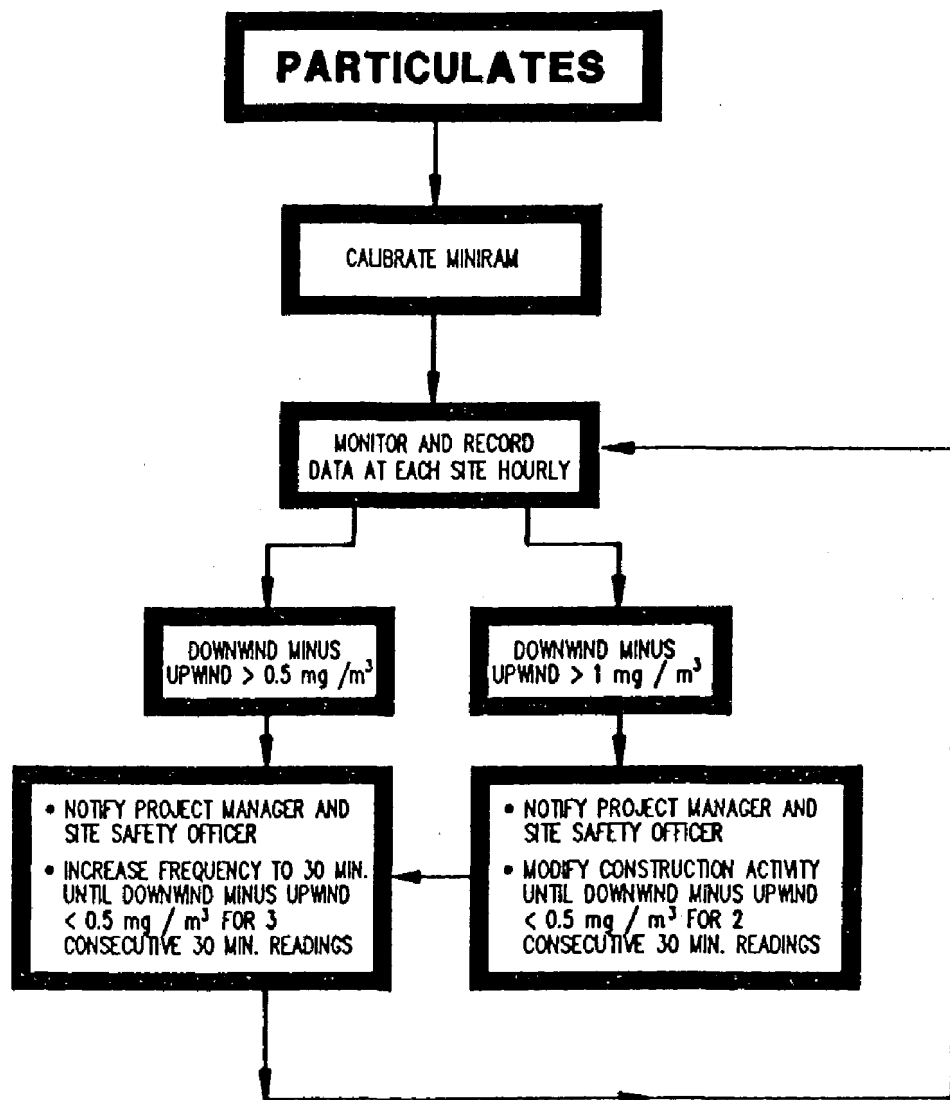


Figure 3. Air Monitoring Plan: Particulates

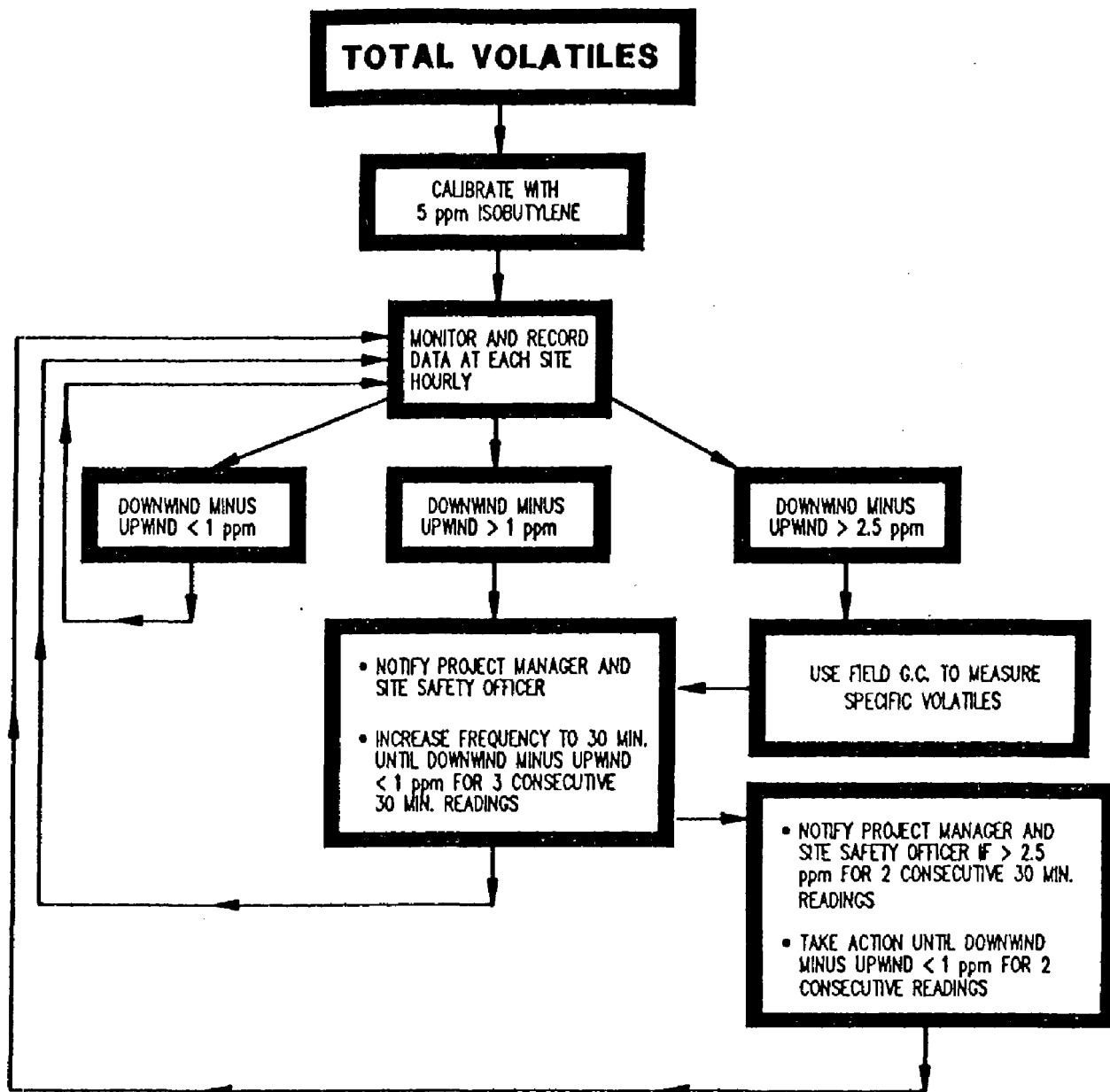


Figure 4. Air Monitoring Plan: Total Volatiles

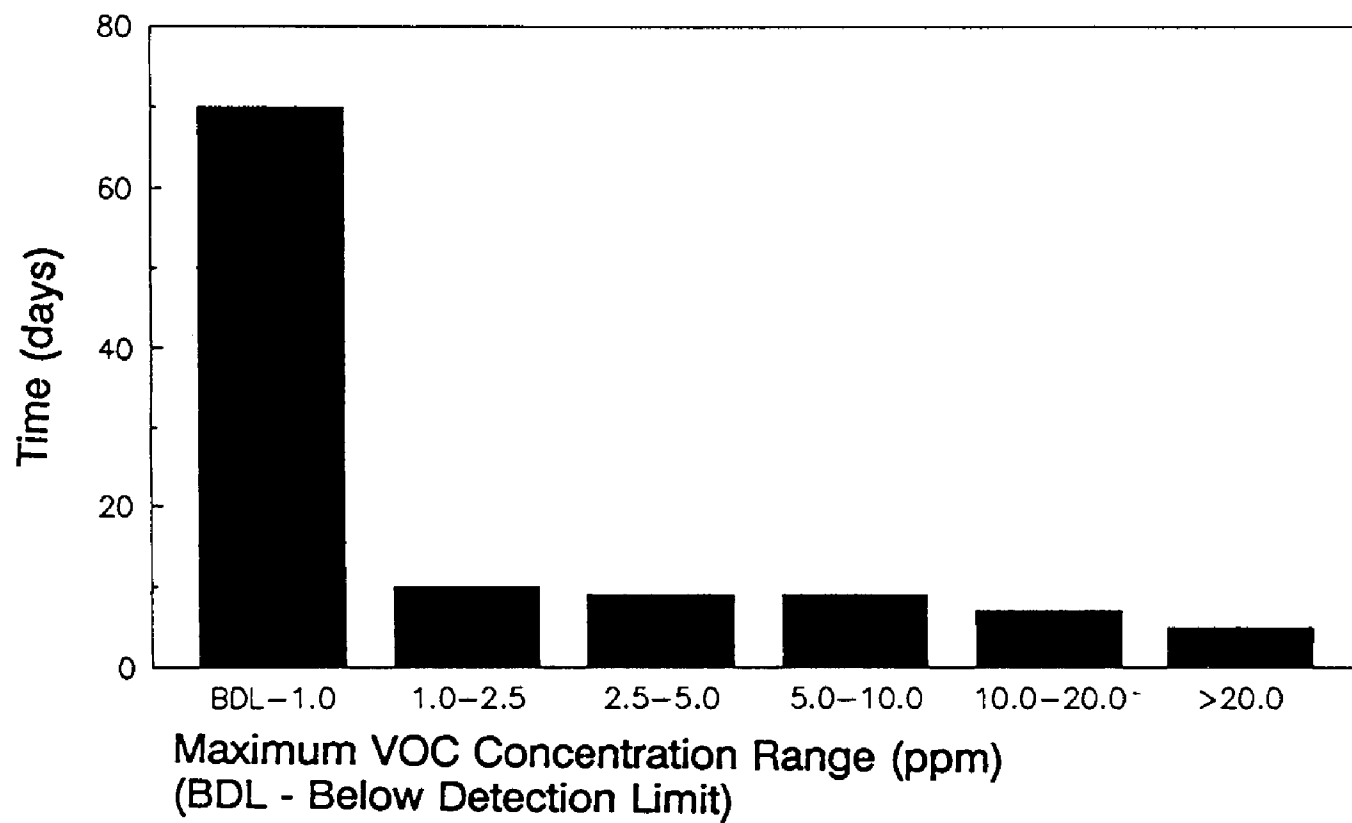


Figure 5. Maximum HNu Readings Histogram

EVALUATION OF METHODS FOR DETECTING DIMETHYL
MERCURY IN AMBIENT AIR AT A SUPERFUND SITE

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Dimethyl mercury, which can be formed by biological detoxification processes for elemental and inorganic mercury, is ten times more toxic than elemental and inorganic mercury, and is more than 10^4 times more volatile than elemental mercury. Thus even trace levels of dimethyl mercury relative to elemental mercury can be of significant concern during soil excavations. This past summer, our organization was requested to develop both a real-time analytical method capable of detecting organomercury compounds at the TLV of 10 ug/m^3 and a time-weighted-average sampling method with a detection limit less than $.25 \text{ ug/m}^3$.

The real-time method was developed built around the Jerome gold film mercury vapor analyzer. The time-weighted-average methods that were initially tested for applicability to dimethyl mercury included use of potassium permanganate based impinger solutions, adsorption/thermal desorption with carbon tubes, and adsorption/thermal desorption with Tenax tubes. Tenax was the only method to give reliable results. Additional work was then done with Tenax to determine safe sampling volumes under field conditions, to estimate approximate detection limits at three local laboratories, and to determine the degree that the detection limits could be increased by using GC/MS-selected ion monitoring versus GC/MS-full scanning.

INTRODUCTION

In June 1989, U.S. EPA Region I requested assistance from the U.S. EPA Environmental Response Team (ERT) because of the potential for dimethyl mercury emissions at the Nyanza Chemical site in Ashland, Massachusetts. The current cleanup of mercury contaminated soils, which were being performed under contract for the Army Corps of Engineers, had then been shut down for three weeks because of the lack of confirmed real-time and time-weighted-average air monitoring methods. Until such methods could be developed, no excavations of mercury laden soils would be allowed by the Corps, by the on-site contractor's industrial hygienist and by the surrounding community. This shut down was costing the government an estimated \$10,000 a day.

The ERT's preliminary assessment of the situation indicated that indeed releases of dimethyl mercury (DMM) could conceivably occur during the remediation of the mercury contaminated, wetland portions of the site. Dimethyl mercury had previously been documented in the literature as a by-product of anaerobic degradation of mercury. The site contained several wetland areas in which such degradation could occur and in which the standing water could act as a potential barrier to DMM escaping to the atmosphere. Therefore, it was conceivable that pockets of DMM vapor could be bound to the subsurface mercury contaminated soils in these areas. In addition, because of its greater than four orders of magnitude higher volatility (vapor pressure of 63 mm Hg at 25°C) relative to elemental mercury and its ten-fold greater toxicity, even minute relative quantities of DMM elemental mercury could be a more significant health concern than the elemental mercury itself - especially considering that the TLV for DMM is 10 ug/m³ or approximately 1 ppb(v).

Because the potential DMM problem was a valid concern and because the lack of any confirmed method was costing the government an appreciable amount of money, the ERT agreed to develop the analytical methods that could be used by the on-site cleanup contractor. Since the sampling and analyses would ultimately be performed by the cleanup contractor and not by the ERT, the developed methods had to meet several criteria normally not found in pure research, method development. First, all time-weighted-average (TWA) sampling methods had to use commercially available sampling equipment and media that could be analyzed by a typical environmental or industrial hygiene laboratory. Second, the real-time analytical methods had to be developed around commercially available portable instruments. Third, both methods had to be selective for DMM over elemental mercury. Fourth, the initial desired sensitivities of the real-time and TWA methods were 10 ug/m³ and 0.1ug/m³, respectively.

The real-time and semi real-time methods that were initially considered included the Jerome gold film mercury vapor analyzer, the Bacharach MV-2 mercury vapor analyzer, and gas chromatography with a photoionization detector (PID). The TWA methods initially considered were absorbent tubes with thermal desorption to a GC/MS and impinger solutions. The two absorbent media evaluated were Tenax and Carbosphere.

REAL-TIME ANALYSES

The Bacharach MV-2 is a UV instrument which responds to compounds such as elemental mercury vapors, that absorb UV light at the wave length of 254 nm. As was expected, initial work with the Bacharach MV-2 at the Region laboratories indicated that the instrument would not respond to DMM. Before any organo-mercury compound can be detected by UV absorption, it must first be converted into elemental mercury. It may have been possible to use an impinger to initially trap the DMM, then convert it to elemental mercury, and finally purge the elemental mercury vapors into the instrument. However, since the prime objective was to develop real-time monitors for field applications, such an impinger setup for the MV-2 was not pursued.

The Jerome meter is a gold film sensor which is set into one side of a wheatstone bridge circuit. Elemental and organo-mercury vapors will contact the gold film and form an amalgam with the gold surface. The formation of the amalgam changes the resistance of the film detector and unbalances the circuit. The result is a signal which is proportional to the mercury vapor concentration. The amalgam is reversible and the gold film returns to its initial resistance once the mercury or organomercury vapors are removed. With elemental mercury the film must be heated in order to revert the amalgam back to pure gold. However, with DMM several runs of clean air are typically sufficient to restore the film surface and will result in a decreased per cent film saturation reading. This decrease in film saturation without heating the film was only seen with DMM and not with elemental mercury.

Initial consultation with the manufacturer's technical staff indicated that the instrument would have a response to DMM but that response had not been reproducible or linear in their experiments. Initial work at the Region 1 laboratory using an instrument configured as per manufacturer's recommended conditions confirmed that the response on the Jerome to DMM to be erratic and unreliable. Subsequent work found that following each positive readings with four successive clean air purges resulted in a linear and reproducible response. Evidently, the methyl groups prevent DMM from forming a true amalgam and cause the DMM-gold interaction to remain a surface phenomenon. Because the response is due to a surface interaction and not a true amalgam, the response was found to be extremely sensitive to the cleanliness of the film's surface. As can be seen in Table I, the maximum sensitivity of the instrument is obtained with freshly cleaned films. As the film becomes dirty from use, the sensitivity will decay over time. As can be seen in Figure 1, this decay is also a function of the concentration of DMM that the instrument has been seeing.

Finally because the methyl groups force the DMM to have certain orientations prior to interacting with the gold film, the overall sensitivity for the instrument is less for DMM than for elemental mercury. Modifications to the instrument were required to increase the sensitivity such that it would read the correct mg/m^3 reading for DMM. These modifications included increasing the sampling flowrate, doubling the sampling time to 20 seconds, and increasing the signal amplification by increasing the resistance between two test points (TP2 and TP3) from approximately 65 Ohms to 98 Ohms.

Selectivity for DMM over elemental mercury was obtained by placing a NIOSH 6000 silver impregnated Chromosorb tube in the inlet of the instrument. These tubes were found to selectively absorb the elemental mercury without affecting the transport of DMM at all. In addition, the suppliers specifications were such that changing tubes did not affect the instrument's calibration by significantly changing the sampling flowrate.

The other "real-time" method, which was suggested by Dr. Tom Spittler, involved the use of a portable GC equipped with a PID detector. The GC was able to detect DMM and apparently had no response for elemental mercury. However, the GC could just barely resolve DMM from benzene. Unfortunately, low ppb(v) levels of benzene would be expected immediately downwind of an area in which diesel-powered earth moving equipment are be used. In addition, the instrument detection limit had a detection limit of approximately 0.3 - 0.5 ppb(v). Therefore, because of the potential problems with benzene interferences and because of the initial successes with the Jerome, the ERT did not pursue this option further. Since that time, researchers at Oak Ridge National Laboratories have continued work with the portable GC using a Tenax based sample preconcentrator.

TWA SAMPLING METHODS

Trapping with Sphero carb followed by thermal desorption using TO-2 conditions did not work. The affinity of Sphero carb for DMM was too great to be overcome by the temperatures being used.

The second method used was an impinger train which was designed to trap the DMM by oxidizing it to inorganic mercury. After samples were pulled, the solutions were taken to a laboratory which analyzed them by cold vapor AA. The impinger solution had the following composition: 5% v/v of 5N H₂SO₄, 2.5% v/v of concentrated nitric acid, 15% v/v of a 5% w/w potassium permanganate solution, and 8% of a 5% w/w potassium persulfate solution. However, after spiking experiments with different flowrates, this method was abandoned. Because of its high volatility and low water solubility, the DMM was being purged through the impinger solutions before it had a chance to be oxidized and thereby immobilized.

Initial work performed in conjunction with Dick Siscanaw of Region I demonstrated better than 85% recoveries of DMM spiked onto the Tenax and then thermally desorbed. Spiked samples sent out to local environmental laboratories indicated that levels as low as 5 ng/tube to 25 ng/tube, could be detected using a GC/MS in the full scan mode. Additional work with one laboratory demonstrated that using selected ion monitoring (SIM) enabled the laboratory to improve the effective detection limits five-fold.

After determining that DMM could be quantitatively desorbed from the tubes and that the GC/MS methods could detect low quantities of DMM, the actual sampling parameters were established. This consisted of spiking 1.5 gram Tenax tubes with vaporized injections of a DMM solution in methanol. On a hot summer day these tubes were then taken on-site and placed directly above dry areas of known high levels of

elemental and inorganic mercury vapors. Three different flowrates were used to pull different volumes of the site air through each set of tubes. The tubes were then taken back to the laboratory for GC/MS analyses. As can be seen in Table II, no breakthrough was seen with the 24 liter sample. This sample volume combined with the worst GC/MS/SIM ng/tube detection limit translated into a method detection limit in the range of 0.2 ug/m³.

CONCLUSIONS

Based upon this work, the following three tier sampling approach has been recommended to the Corps of Engineers for monitoring DMM in the air during the Nyanza cleanup operations. The first tier involves the use of the Jerome gold film analyzer with the silver impregnated chromosorb pre-filter to obtain real-time readings for DMM. Care should be taken to insure that the instrument's calibration is checked and re-adjusted throughout the day. Whenever a positive reading is obtained by the Jerome, a confirmation air sample should be taken and concentrated approximate 5 - 10 fold for analysis by the PID portable GC, the second tier. The third tier would consist of both perimeter Tenax samples and at least work zone Tenax sample for subsequent off-site analyses. As more sensitive and selective GC detectors, such as the atomic fluorescence detector, are developed and become more common, then these instruments would be appropriate as replacement tier 2 analytical methods.

TABLE I. JEROME METER RESPONSE AND HEAT CYCLES

DMM STANDARD @ 6.4 ppbv

Time (minutes)	meter reading
Start - 0	0.040
End - 345	0.014
After heat cycle -	0.038
% recovery -	95.0%

DMM STANDARD @ 13.7 ppbv

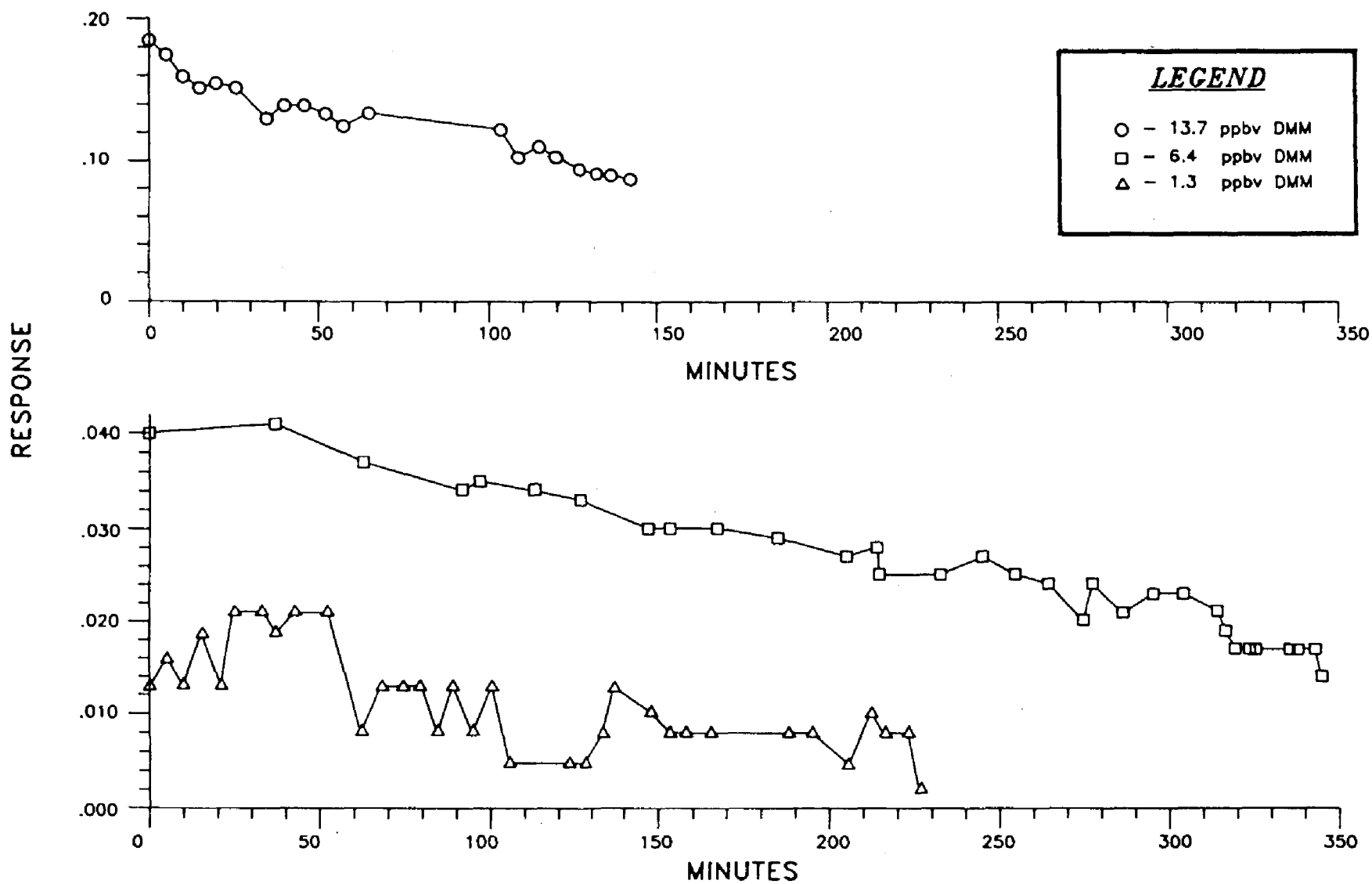
Time (minutes)	meter reading
Start - 0	0.188
End - 120	0.120
After heat cycle -	0.177
% recovery -	94.1%

NOTE: Above standards analyzed at 5 minutes intervals until end time.

TABLE II. TENAX TUBE BREAKTHROUGH RESULTS

Tube #	ng DMM spiked	Volume of Air Pulled Thru Tube	ng DMM GC/MS Data	% Recovery
1	2000	95	< 25	0
2	2000	95	57	2.85
3	2000	48	970	48.5
4	2000	48	1200	60.0
5	2000	24	1800	90.0
6	2000	24	2500	125.0
7	2000	0	1900	95.0
8	2000	0	1900	95.0
9	2000	0	2000	100.0
10	0	0	< 25	--
11	0	0	< 25	--

FIGURE 1. DECAY OF DIMETHYL MERCURY RESPONSE OVER TIME AS OBSERVED AT THREE SEPARATE CONCENTRATIONS.



HAZARDOUS WASTE TSDF PM₁₀ EMISSIONS

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This paper summarizes a guidance document that provides regulatory and industrial personnel with necessary information to identify sources of contaminated fugitive PM₁₀ emissions, estimate the magnitude of emissions, select viable control measures, and estimate the effectiveness of those measures. Sources of particular concern are landfills, land treatment, waste stabilization, dry surface impoundments, and roads. Included in the document are detailed descriptions of PM₁₀ emission models and control performance models that apply to these sources. These models were developed by plume profiling of representative sources before and after control application using monitoring techniques described in the paper. Because of the similarity between various Superfund site activities and treatment, storage, and disposal facility (TSDF) operations, these technological approaches are in large part transferrable to Superfund sites.

Introduction

Earlier EPA studies have evaluated fugitive particulate matter (PM) emissions from hazardous waste Treatment, Storage, and Disposal Facilities (TSDFs). Sources of particular concern are landfills, land treatment, waste stabilization, dry surface impoundments, and roads. These sources of emissions are regulated by a site-specific permitting system for TSDFs that has been established under the authority of the Resource Conservation and Recovery Act (RCRA).

This paper summarizes a guidance document¹ that provides regulatory and industrial personnel with sufficient information to identify sources of contaminated fugitive PM emissions, estimate the magnitude of emissions, select viable control measures, and estimate the effectiveness of those measures. The PM particle size fraction of interest, designated as PM₁₀, consists of particles with an aerodynamic diameter equal to or less than 10 micrometers (μm).

Major TSDF Source Categories

The following source categories may be identified in relation to TSDFs:

- Paved and Unpaved Roads
- Open Waste Piles and Staging Areas
- Dry Surface Impoundments
- Landfills
- Land Treatment
- Waste Stabilization

Unlike the other source categories listed above, the emissions from paved and unpaved roads at hazardous waste (HW) treatment, storage, and disposal facilities (TSDFs) are not due to an identifiable unit operation at each facility. Rather, the roads serve as "linkages" between the various unit operations (e.g., access from the gate to the active disposal area, transfer of solidified wastes from the solidification unit to a disposal unit, etc.).

Particulate emissions occur whenever a vehicle travels over a paved or unpaved surface, such as a road or an area proximate to a TSDF unit operation. Note that travel areas adjacent to TSDF operations may have a high potential for contaminated particulate emissions, with the potential inversely related to the level of "good operating practices" at the unit operation. In the case of paved roads, emissions originate with (a) resuspension from vehicle tires and undercarriages or (b) material deposited onto the surface. Material tracked onto the road from potentially contaminated travel areas surrounding TSDF operations will be spread along the road's length and eventually some of that material will become airborne. While track-on material is usually more noticeable on paved roads, the spreading of potentially contaminated material also occurs on unpaved surfaces.

Past surveys of TSDFs have in fact indicated that unpaved road surfaces at these types of facilities may have RCRA metal and semivolatile organic contamination levels essentially comparable to levels in samples taken from process-related surfaces (e.g., landfill areas, areas surrounding a stabilization/solidification unit, etc.).² Because of the large volume of traffic associated with many facilities, those surveys suggest that general vehicular traffic on plant roads may be the principal source

of contaminated emissions associated with TSDFs. While the source of road surface contamination cannot be definitively identified, the two most likely causes are (a) spillage from vehicles hauling the waste or (b) "track-out" of material from surfaces surrounding process operations at the TSDF.

In many respects, control measures commonly applied to alleviate "gross" (i.e., uncontaminated) particulate emissions may actually compound contaminated emissions. For example, travel areas surrounding an active TSDF unit operation may be watered to control emissions. However, watering tends to increase the amount of track-out onto an adjacent paved road, and the deposited material soon dries out and becomes airborne under normal plant traffic conditions.

Each section of the guidance document begins with an overview of a specific source category, describing emission characteristics and mechanisms. Following this, available emission factor models (Table I) are presented to provide a basis for analyzing the operative nature of control measures. Next, demonstrated control techniques are discussed in terms of estimating efficiency and determining costs of implementation. Suggested regulatory formats explain the "philosophy" used in implementing the preceding technical discussions in viable regulations and compliance actions.

Particulate Emission Factor Models

In developing particulate control strategies for "traditional" pollutant concerns (i.e., to meet National Ambient Air Quality Standards [NAAQS]), gross particulate emissions from open sources are estimated using the predictive emission factors presented in Section 11.2 of EPA's "Compilation of Air Pollutant Emission Factors" (AP-42).³ These factors cover the generic source categories:

- Unpaved travel surfaces
- Paved travel surfaces
- Exposed areas (wind erosion)
- Materials handling

Note that these factors are updated periodically and that users of this document should use updated factors as they become available.

These emissions factors share many common features. For example, the models are formulated as empirical expressions that relate variations in emission factor (e) to differences in the physical properties (p) of the material being disturbed and the mechanical energy (m) responsible for the generation of particulate according to the general form:

$$e = Kp^a m^b \quad (1)$$

As empirical models, open dust source emission factors have adjustable coefficients (K,a,b) that reflect relationships determined from actual open dust source testing.

Much of cited guidance document centers on the application of the open dust factors to estimate particulate emissions from permitted TSDF units. Table I summarizes the applicability of AP-42 emission factor

models to TSDF source categories. Estimation is accomplished according to the general model form:

$$R = \sum_{j=1}^n \alpha_j \cdot e_j \cdot A_j \quad (2)$$

where: R = emission rate of contaminated airborne particulate (kg/yr) for a given TSDF, consisting of n identifiable unit operations

α_j = fraction of contaminant in particulate emissions for the j th operation ($\mu\text{g/g}$); for uncontaminated particulate emissions, $\alpha_j = 0$

e_j = emission factor(s) (mass/source extent)

A_j = source extent(s) (source dependent units)

This approach is analogous to that used by MRI in recent work on estimation of emissions from surface contamination sites.⁴ The approach is also consistent with techniques used in air pollution assessments.

In the TSDF context it is important to recognize the following:

1. The α term refers to the "level of contamination" and is usually represented as the concentration (e.g., $\mu\text{g/g}$) of the metal(s) or organic compound(s) of concern in the disturbed material.
2. Permitted TSDF units may consist of multiple, identifiable unit operations; in the case of landfills, for example, unit operations include loadout of bulk hazardous waste, loadout of temporary cover, lift construction, and general vehicle traffic proximate to the landfill face.
3. The major assumption implicit in Eq. (2) is that TSDF processes that generate particulate emissions can be adequately represented by existing open dust source emission factor models.

Item 2 above is relatively straightforward and is demonstrated in the individual chapters. Items 1 and 3 require further clarification as given below.

Specification of the level of contamination (α) probably is the single most difficult aspect of applying the emission factors. For a given TSDF source, "representative" value(s) of α may depend upon a number of factors including principally:

1. The nature of waste streams handled and whether the wastes are metal-containing or organic waste streams.
2. Operational practices that influence the availability of waste material for entrainment into the atmosphere.
3. The age of the facility to the extent that it reflects "residual" contamination associated with long-term disposal and typical waste stream volumes.

Note that the term *representative* is used here to connote a long-term value, such as an annual mean, that adequately defines α over the entire TSDf source.

There are essentially two methods for specification of α . The preferred method is through source-specific sampling and analysis (S&A). In some cases it may be feasible to develop estimates of α for a specific source based on existing information other than actual S&A data. In general, these estimates should be developed from the perspective of a "worst-case scenario," because of the greater uncertainty involved. In other words, they should be conservatively high and thus tend to protect against any potential underestimation of risk associated with particulate emissions.

The principal sources of information for worst-case estimates are expected to be:

1. Waste manifests and any "tracking" information that a facility routinely generates to characterize its receipts.
2. Conversations with facility personnel.

Because the emission factor models are empirical expressions, in a strict sense their degree of applicability relative to TSDf sources is related to the degree of compliance with two conditions:

1. How closely a given TSDf unit operation resembles the source conditions underlying test data used in development of the emission factor.
2. How closely the physical characteristics of the disturbed material resemble those tested in development of the emission factor.

Based on surveys described in reference 2, the general conclusion is that TSDf unit operations are reasonably comparable to those tested in development of the emission factor relationships.

Results of the surveys described in reference 4 also clearly point out that the physical characteristics of waste and disturbed surface materials at TSDfs do not always conform closely to those materials tested in development of the emission factors. More specifically, the moisture and/or "oily nature" of waste streams may be markedly different from the dry, finely divided materials upon which the field tests were performed. The current emission factor models do not fully account for the inherent mitigation provided by the physical binding effect of oily substances, which may add conservatism to the predictive emission rates. However, at any given facility, the potential for increased spreading of material may offset this conservatism.

Preventive and Mitigative Control Options

Typically, there are several options for control of fugitive particulate emissions from any given source. This is clear from the mathematical equation used to calculate the emissions rate:

$$R = A e (1 - c) \quad (3)$$

where: R = estimated mass emission rate

A = source extent (i.e., surface area for most open dust sources)

e = uncontrolled emission factor, i.e., mass of uncontrolled emissions per unit of source extent

c = fractional efficiency of control

To begin with, because the uncontrolled emission rate is the product of the source extent and uncontrolled emission factor, a reduction in either of these two variables produces a proportional reduction in the uncontrolled emission rate.

Although the reduction of source extent results in a highly predictable reduction in the uncontrolled emission rate, such an approach in effect usually requires a change in the process operation. Frequently, reduction in the extent of one source may necessitate the increase in the extent of another, as in the shifting of vehicle traffic from an unpaved road to a paved road.

The reduction in the uncontrolled emission factor may be achieved by process modifications (in the case of process sources) or by adjusted work practices (in the case of open sources). The degree of the possible reduction of the uncontrolled emission factor can be estimated from the known dependent of the factor on source conditions that are subject to alteration. For open dust sources, this information is embodied in the predictive emission factor equations for fugitive dust sources as presented in Section 11.2 of EPA's "Compilation of Air Pollutant Emission Factors" (AP-42).²

Control techniques can be divided into two broad categories--preventive and mitigative. Although differences between the two are not always clear, in general, preventive measures involve techniques that reduce source extent or improve mechanical source operations relative to the generation of particulate emissions. By contrast, mitigative techniques typically focus on altering the surface/material conditions that constitute the source of particulate emissions.

In the TSDF context an example of a preventive control technique involves traffic routing of haul truck vehicles in the staging areas proximate to an active landfill face. The objective of traffic routing is to minimize the contact between vehicle wheels and waste material and thus limit the potential spreading of contamination material to the facility roadways. In this fashion the source extent of contaminated material is effectively reduced.

An example of a mitigative measure involves the application of water to unpaved travel surfaces in order to suppress the entrainment of gross or contaminated particulate by vehicle traffic. The important point here is that relative to contaminated particulate, it is assumed that the roadways are characterized by some (albeit unknown) level of contamination (α) associated with long-term waste disposal operations, and that the objective is to minimize the entrainment of this material into the atmosphere.

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TABLE I
APPLICABILITY OF AP-42 EMISSION FACTORS

TSD source	Emission model					
	Unpaved roads	Paved roads	Materials handling	Ind. wind erosion	Dozer operations	Land tilling
Paved/unpaved roads	X	X				
Open waste piles/staging areas			X	X		
Dry surface impoundments			X	X		
Landfills	X		X		X	
Land treatment	X				X	X
Waste stabilization		X	X	X		

A METHODOLOGY FOR IDENTIFYING AND RANKING TOXIC AIR POLLUTANTS AT SUPERFUND SITES

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ABSTRACT

This paper describes a methodology for identifying toxic air pollutants of concern at Superfund sites, as a preliminary step to developing an air toxics Statement-of-Work for USEPA's Contract Lab Program. The methodology ranks the toxic air pollutants of concern in order of relative importance, as determined by frequency of occurrence at Superfund sites and potential for threat to human health.

A master list of 260 potential toxic air pollutants was formed from USEPA's Hazardous Substances Priority Lists and other authoritative lists. Primary criteria for selection of available data describing the target compounds were toxicity, carcinogenicity and potential for human exposure at or in the vicinity of Superfund sites. Secondary criteria included consideration of regional, state and local regulatory needs and availability of existing analytical methods and reference standards. In evaluating the acceptability of candidate analytical methods, a reference ambient level was determined for a number of target compounds lacking unit risk estimates. Data describing these criteria were arrayed in a computer spreadsheet and processed in a ten-term algorithm, to arrange the toxic air pollutants in order of priority. Each algorithm term described one of the primary or secondary criteria and was assigned a relative weight by USEPA.

INTRODUCTION

As specified in the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) and the Superfund Amendments and Reauthorization Act (SARA), EPA has the responsibility for assessing the potential for air emissions and air quality impacts prior to and during Superfund hazardous waste site cleanup. CERCLA and SARA mandate the characterization of all contaminant migration pathways from waste to the environment and of the resulting environmental impacts. In particular, a remedial investigation must provide data on air emissions from the site in undisturbed and disturbed states. CERCLA and SARA also require the development of data that are "necessary and sufficient" to characterize the "nature and extent" of contamination on site. Consequently, regulatory agencies, site managers and Remedial Program Managers (RPMs) must develop site-specific objectives in characterizing air emissions at these sites.

To address the absence within EPA of standardized sampling and analytical procedures for characterizing air emissions from pre-remedial/removal activities at Superfund sites, EPA's Office of Emergency and Remedial Response (OERR) is developing a "Statement-of-Work for Analysis of Air Toxics at Superfund Sites."

One of the early tasks in the development of the Statement-of-Work is the preparation of the target compound list (TCL), a prioritized list of compounds for which analytical protocols are to be included in the Statement-of-Work. The TCL comprises compounds most commonly found at Superfund sites and which pose the most significant threat to human health, and which are likely to enter the ambient air at Superfund sites. Many of the target compounds do not have EPA published unit risk values. Unit risk values are significant because they allow the calculation of ambient levels which relate to any specific risk level of concern (e.g., 10^{-6}) for carcinogens, data which in turn predict the required level of analytical detection limits for many of the analytical data uses. If substances are to be the target of sampling activities at NPL sites, it is clearly desirable to have sampling and analytical methods which are capable of detecting concentrations of substances at these levels. To compensate for the lack of unit risk estimates for many target compounds, Reference Ambient Levels (RALs) were developed to represent the lowest ambient concentration of concern at Superfund sites.

DEVELOPMENT OF A RANKED TARGET COMPOUND LIST

Since no generally accepted list of air toxics at Superfund sites is available, the first task in the development of the ranked TCL is preparation of a master list of candidate compounds. The Hazardous Substances Priority Lists* were selected as the starting point in preparing this list.

*CERCLA requires that the USEPA and the Agency for Toxic Substances and Disease Registry jointly list in order of priority, hazardous substances which are most commonly found at NPL facilities and which the agencies determine are posing the most significant potential threat to human health.

It was necessary to augment the Hazardous Substances Priority Lists of 200 of the most hazardous substances found at Superfund sites because these lists were compiled with only minimal consideration of the air pathway. Accordingly, 60 air toxics compounds were selected from other authoritative lists.

After the master list was compiled, a straightforward method was developed to rank these compounds in order of importance as air toxics at Superfund sites. General considerations in developing the ranking scheme were:

- Frequency with which compounds were mentioned in a survey of EPA Regions.
- Frequency with which compounds have been found at Superfund sites.
- Compounds which present a risk of exposure by inhalation and which are highly toxic or carcinogenic.
- Frequency with which compounds are requested under Federal or state regulations (ARARs and TBCs) to meet cleanup goals.
- Availability of sampling/analysis methods and reference standards for the TCL.
- Relative volatility of the candidate compounds.
- Availability of health-based data (unit risk, reference doses and acceptable ambient levels) for the TCL.

These criterias can be grouped into three major areas; health effects, regional needs, and potential for human exposure.

HEALTH EFFECTS

Health effects were addressed in detail through a variety of descriptive indicators, including unit risk factors, cancer potency slopes, and reference dose values, and other less specific descriptors in cases where data of primary quality were not available.

In considering health effects we used available data developed by USEPA's Pollutant Assessment Branch (PAB) and generally contained in the list of unit risk factors for the inhalation of carcinogenic air contaminants. This list is maintained by PAB for air assessments performed with EPA's Office of Air Quality Planning and Standards (OAQPS). The PAB also maintains a separate list of compound "cancer potency slopes" which in most cases are based upon ingestion routes of exposure. Because in many cases these cancer potency slopes have been and will continue to be converted to inhalation factors for use in air toxics risk assessments, we included these data in our assessment and ranking of health effects. For non-carcinogens we referred to lists maintained by EPA's non-carcinogen workgroup. These are compounds for which EPA has determined a need for the development of "reference dose" (RfD) values. Reference dose is used by USEPA as threshold value in evaluating non-carcinogenic health effects.

For other compounds on the list not described by any of these data, various health effects indicators such as threshold limit values and reportable quantity data from SARA Title III were used. In all cases, the end product of the health effects data assessment was a health effects ranking number between one and ten, so that each compound on the master list could be ranked on a common basis. Health effects was designated the most important of the ten ranking criteria, and was accordingly most heavily weighted in the ranking scheme.

REGIONAL NEEDS

In assessing regional needs for sampling guidance and analytical methods for specific air toxics, we relied on responses to the USEPA Regional air toxics survey conducted in March, 1989. Many regions provided lists of important air toxics compounds; frequency with which specific compounds appeared on these various lists was the second most important ranking criteria.

Of next major importance as an indicator of regional needs is the regulation of specific air toxics compounds by the various states. Since the limited scope of the project precluded an in depth review of all applicable state regulations, we relied on the data base developed by the National Air Toxics Information Clearinghouse as an indicator of state regulatory activity for specific air toxics chemicals. For various states regulating on the basis of acceptable ambient levels (AALs), frequency of occurrence of regulations for specific chemicals was the third most important ranking criteria.

Frequency of occurrence on various credible lists of hazardous materials was also considered to be a useful ranking indicator. The California Air Resources Board (CARB) publishes a "Lists of Lists" which shows the frequency with which specific chemicals are listed in 12 authoritative lists of hazardous chemicals. The New York Air Guide I also categorizes specific air toxics compounds as high, medium, or low toxicity. SARA Title III, Section 302 also lists hazardous pollutants. Frequency of occurrence in each of these lists was used as an indicator of relative importance of these compounds, occupying the 4th, 5th, and 8th positions in order of importance of ranking criteria.

POTENTIAL FOR HUMAN EXPOSURE

Indicators for the potential for human exposure were incorporated by considering both the frequency of occurrence at Superfund sites and the volatility of each of the listed compounds. Frequency of occurrence at Superfund sites was obtained directly from the August 1988 list entitled "Frequency Distribution of Substances Present at Final and Proposed NPL Sites." Each target compound was assigned a volatility ranking number between 0.5 and 3, derived from boiling point and/or vapor pressure data as available. These indicators are generally considered to represent potential for human exposure through the air pathway at Superfund sites and were assigned the 6th and 7th positions in the ranking scheme.

AVAILABILITY OF ANALYTICAL METHODS AND REFERENCE STANDARDS

The 9th and 10th weighing positions were assigned to availability of analytical method and standard, respectively. We felt that for marginal compounds the availability or lack of analytical methods and reference standards could be a factor in the decision to include or exclude such compounds from the priority target compound list.

In evaluating the suitability of available analytical methods we decided to compare method detection limits with ambient levels of concern determined by unit risk values and an acceptable risk of 10^{-6} .

Many of the substances of the 257 on the original TCL do not have EPA published unit risk values. To provide a comparable measure of ambient level of concern for these target compounds, we devised the reference ambient level (RAL). RALs were designed to be an approximation of potential Applicable or Relevant and Appropriate Requirements (ARARs) or "To-Be-Considered" materials (TBCs) in establishment of air cleanup standards for remedial actions at National Priority List (NPL) sites. If substances are to be the target of sampling activities at NPL sites, it is clearly desirable to have sampling and analytical methods which are capable of detecting concentrations of substances at these levels.

The concentration-based levels of concern were obtained from state and local air toxics programs. There has been much controversy over appropriate methodologies for determining acceptable ambient levels (AALs). Many states use Threshold Limit Values (TLVs) divided by a safety factor, despite the fact that the publisher of TLVs, the American Conference of Government and Industrial Hygienists, explicitly recommends against the use of TLVs for such an application. Nevertheless, under USEPA's developing guidance for ARARs and TBCs, any state regulation or guidance potentially could be used as the basis of an air clean-up standard, regardless of the basis of that regulation or guideline. Accordingly, it is important to know what states currently are using as AALs to determine what sampling and analytical methods are needed at NPL sites. Having an evaluation of current practice for AALs appears to be the best starting point for determining an appropriate approach for recommending practical sampling and analytical methods.

Current practice for AALs, however, is not uniform from state to state. In order to focus this effort, we decided to concentrate on states with the most sites on the NPL. Each state was contacted for documentation on their methodology for developing AALs, along with a listing of pollutants and applicable AALs (if one exists). Some of the states provided methodologies only, and calculations of AALs based on designated input data (such as TLVs) was necessary.

AALs were then tabulated by averaging time, and if more than one state regulates a single pollutant for the same averaging time, AALs were presented as a range. No conversion factors were used to modify AALs from one averaging time to another, because applicable ARARs and TBCs arguably must use the state or local guideline as it exists. RALs based on the lowest concentration of any 10^{-6} concentration, modified RfD, or AAL

were then tabulated.

In all cases, if an Acceptable Air Risk (AAR) was given, it was selected as the RAL. If no AAR value was available, the most restrictive value represented by the states and the corresponding Reference Dose (RfD) value was selected. In cases where neither an AAR nor RfD was available, the most restrictive state value was selected as the RAL.

Information used to develop the RAL table was obtained from the states of California (Bay Area), Connecticut, Indiana, Maryland, Massachusetts, Michigan, New York, and Wisconsin. The Reference Doses (RfD) were taken from USEPA's IRIS system.

DESCRIPTION OF RANKING PROCESS

To complete the ranking process, each of the candidate chemicals on the expanded master list was entered into a Lotus 1-2-3 spreadsheet and arrayed with corresponding numerical data describing each of the ten ranking criteria. An algorithm was devised which would position the maximum value of each of the ranking criteria terms in its relative weighted position. The algorithm, the ranges of the numerical data in the spreadsheet, and the relative maximum term values are shown in Figure 1. For example, AOB designated Health Effects as the most important of the descriptive criteria and was accordingly ranked number one (1); Availability of a Reference Standard was the least important, ranked number ten (10). These rankings are shown in Figure 2, column 2. For convenience in developing a ranking index (RI) algorithm, the ten (10) ranking parameters were assigned corresponding maximum values of the algorithm terms representing these parameters. For Health Effects, a maximum term value of 100 was selected, while for Availability of Reference Standard a maximum term value of 30 was selected. Intermediate term values for other descriptors were selected so that each algorithm term representing a descriptor was retained in the relative positions specified by AOB.

Data in the Lotus 1-2-3 spreadsheet were arrayed in various ways for the various descriptors. For Health Effects, each chemical was assigned an index value between 1 and 10, ten being the maximum value of the health effect descriptor and representing the greatest level of health hazard. For Availability of Reference Standard, each chemical was assigned an index value between 0 and 2, 0 representing no standard available and 2 representing availability of an EPA-certified standard. The algorithm constant was derived by dividing the maximum term value by the maximum numerical index value arrayed in the spreadsheet. For health effects, the algorithm constant was 10 ($100/10 = 10$), while for Availability of Reference Standard, the algorithm constant was 15 ($30/2 = 15$).

As shown in Figure 1, the ranking index was designated as the sum of the descriptor terms, with a maximum summed value of 645. Figure 2 illustrates the scoring for vinyl chloride, the highest ranked chemical on the TCL with a score of 515. Table 1 lists the data sources used in development of the target compound list.

CONCLUSIONS

Although no absolute measure of the validity of the ranking methodology is available, our preliminary conclusion at this stage is that the list adequately predicts the range of compounds likely to be encountered at Superfund sites. We also feel that it represents the best compromise to providing a target compounds list which addresses health effects, regional needs, potential for human exposure, and regulatory requirements. By considering unit risk estimates and RALs in comparison with analytical detection limits for priority target compounds, it was possible to select appropriate general analytical methods for nearly all target compounds.

As greater experience is gained in analysis of air toxics at Superfund sites, changes to this target compound list and possibly to the general analytical protocols are expected. We are, however, confident that we can move forward in development of the Statement-of-Work with the expectation that the initial Statement-of-Work for Superfund site air toxics analysis will adequately address the program requirements.

DISCLAIMER

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TABLE 1
LIST OF DATA SOURCES
FOR DEVELOPMENT OF TARGET
COMPOUND LIST

- EPA Health Effects Summary Tables
- PIPQUIC (IRIS) Data Base
- March '89 Survey Responses
- New York Air Guide II
- California Air Resources Board List of Lists
- SARA Title III Section 313 List
(and Reportable Quantity Table)
- National Air Toxics Information
Clearing House Report on Air Toxics
Activities
- Frequency Distribution of Substances Present
at Final and Proposed NPL Sites
- Superfund Public Health Evaluation Manual
- USEPA Technical Guidance for Hazards Analysis
- CRC Handbook of Chemistry & Physics
- Merck Manual

FIGURE 1 RANKING INDEX (RI)
ALGORITHM AND DERIVATION OF TERM VALUES

$$RI = 10G + 11.3B + 120M + 7.5D + 23.3F + 10K + 20L + 40E + 35C + 15J$$

Data Source			Lotus 1-2-3 Spreadsheet Range of Numerical Data			Derived Constant for Algorithm (a ÷ b)
Descriptor	Rank ¹	Selected Max. Value of Descriptor (a)	Algorithm Variable	Min. Value	Max. Value (b)	
Health Effects Index	1	100	G	1	10	10
Number of Listings in Survey Responses	2	90	B	0	8	11.3
Frequency of Listings in State AAL Regs. ²	3	80	M	0	0.667	120
Number of Entries in CARB List of Lists	4	75	D	0	10	7.5
Category in NY Air Guide	5	70	F	0	3	23.3
Frequency of Occurrence at NPL Sites ³	6	65	K	0	6.5	10
Volatility Index	7	60	L	0.5	3	20
Listing in SARA Title III	8	40	E	0	1	40
Availability of Analytical Method	9	35	C	0	1	35
Availability of Reference Standard	10	30	J	0	2	15
Maximum value of Algorithm		645				

¹ relative importance of descriptor, as specified by AOB, HSED, OERR

² numerical data expressed as decimal fraction

³ numerical data expressed as decimal fraction x 100, for multiple listings only

**FIGURE 2. SAMPLE CALCULATION
FOR VINYL CHLORIDE**

Value ¹ of Variable in Algorithm	Descriptor	Vinyl Chloride Term Value ²
G = 4	Health Effects Index	40
B = 8	Frequency of Listing in Survey Responses	90
M = 0.5	Frequency of Listing in State AAL Regs.	60
D = 10	Number of Entries in CARB List of Lists	75
F = 3	NY Air Guide List	70
K = 1.51	Frequency of Occurrence at NPL Sites	15
L = 3	Volatility Index	60
E = 1	Listing in SARA Title III	40
C = 1	Availability of Analytical Method	35
J = 2	Availability of Reference Standard	30
Total Algorithm Value for Vinyl Chloride		515

$$\begin{aligned}
 \text{RI} &= 10G + 11.3B + 120M + 7.5D + 23.3F + 10K + 20L + 40E + 35C + 15J \\
 &= 10(4) + 11.3(8) + 120(0.5) + 7.5(10) + 23.3(3) + 10(1.51) + 20(3) + 40(1) + 35(1) + 15(2) \\
 &= 40 + 90 + 60 + 75 + 70 + 15 + 60 + 40 + 35 + 30 \\
 &= \underline{515}
 \end{aligned}$$

¹ values for vinyl chloride terms from Lotus 1-2-3 spreadsheet

² rounded off to nearest whole number

**AIR TOXICS CONSIDERATIONS
AT AN ACTIVE
FIREFIGHTER TRAINING FACILITY**

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This paper describes the concerns, study approach and the results of air sampling at an active firefighter training facility. Air sampling was performed of the buildings, mockup structures, and gas wells (installed near mock up structures) during live burns for parameters including VOCs and combustible gas.

The concerns related to the potential for vapor emissions from site contamination and methane from an adjacent landfill. Groundwater contamination was likely a result of previous use of dry wells. During previous site investigations, combustible gas was detected in groundwater wells, triggering concern for the safety of on-site personnel, and the safety of firefighters using the training facility.

The study was developed to evaluate the presence of gases and vapors in the buildings and the potential for any effects of live burns on gas and vapor levels. The air sampling program included organic vapor collection on adsorbent tubes, and use of combustible gas meters, photoionization detectors, and a portable GC. Since site conditions and concerns may be representative of fire training facilities throughout the country, the air sampling approach utilized is applicable to similar studies.

INTRODUCTION

Fire training facilities provide a valuable service to communities throughout the country by providing a means of training and exposing firefighters (in a controlled setting) to the harsh and dangerous realities of fighting fires. Unfortunately some of these facilities may be on sites contaminated from spillage of waste liquids or loss of fuels through inadequate drainage systems. The presence of contamination may pose a threat to air quality and a potential hazard to personnel who occupy and use such facilities.

This paper describes the concerns, study approach and the results of air sampling at an active firefighter training facility. Air sampling was performed of the buildings, mockup structures, and gas wells (installed near mock up structures) during live burns. Parameters of interest included selected volatile organic compounds (VOCs) and combustible gas.

BACKGROUND

The site houses fire training and administrative functions. The facility is occupied by full and part time administrative and maintenance personnel and periodically (during training sessions) by instructors and students from over 50 volunteer fire districts. Advanced training consists of classroom and controlled live burn exercises.

Structures on the 10 acre plus site include a number of buildings i.e., administration, first aid, classroom, pumper test, maintenance and pump house. In addition training facilities include building mockups (dwelling, commercial, and tower) and fire extinguisher, open pit, tower/ladder, and propane training areas.

Adjacent to the site is a municipal solid waste landfill that has landfill gas control systems (i.e., recovery, flaring and venting) that extract gas from the landfill and burn it for power generation, flare it for disposal and vent it to control subsurface migration, near the fire training site.

Ground water investigations of the site indicated the presence of floating product (chiefly No. 2 fuel oil) resulting from past use of dry wells. Trace contaminants related to fuels and solvents detected in ground water were the focus. These included benzene, toluene, xylenes, carbon disulfide, vinyl chloride, methylene chloride, 1,1-dichloroethene, 1,1-dichloroethane, trans-1,2-dichloroethene, 1,1,1-trichloroethane, trichloroethene, tetrachloroethene, chlorobenzene, ethylbenzene, 2-butanone and acetone. Concern was raised when significant levels of combustible gas were detected in several of the ground water monitoring wells.

Maintenance personnel at the site were reported to have been exposed to noxious gases, suspected as originating from the landfill. Other reports indicated occasional instances of unusual fire conditions in the mock up buildings during training.

Concern over potential hazards associated with air quality onsite led to questions related to safe operation of the facility, i.e.,

- are toxic vapors or gases present at the facility at potentially harmful levels;
- can explosive conditions arise from combustible gas accumulation in the buildings; and

- is there migration of potentially harmful or dangerous vapors or gases from the ground into the mockup buildings during fire training exercises?

APPROACH

The diversity of the concerns and the different variables associated with routine site activities called for an approach consisting of careful planning and clearly identifying the study objectives (1). The identified objectives of this study were to:

- quantify airborne concentrations of volatile organic contaminants (VOCs) during various site activities, and assess potential hazards to personnel and firefighters;
- develop a program for continued operation of the facility while reducing exposures, consisting of a combination of appropriate engineering controls, administrative procedures and/or continuous site monitoring; and
- establish a framework for emergency and contingency planning.

A number of tasks were performed to meet these objectives, that included:

- air quality monitoring with various meters (oxygen, combustible gas, photoionization and organic vapor detectors);
- air quality screening with a Photovac field gas chromatograph;
- air sampling with adsorbent tubes with laboratory analysis for VOCs;
- installation of gas monitoring wells;
- measurement of differential well pressure and temperature during fire training activities and screening the constituents of soil gas;
- observation of administrative, classroom, and fire training activities; and
- interviewing of various site personnel regarding standard procedures and site history.

Grab (air) samples (almost real-time) were analyzed for six VOCs using a Photovac (GC Model 10S50) portable gas chromatograph onsite to monitor air quality over a 72-hour period. The calibration gas used with the Photovac GC consisted of 1 ppm each of vinyl chloride, methylene chloride, 1,1-dichloroethene, trichloroethene, benzene and tetrachloroethene, based upon presence in ground water and relative toxicity.

In addition, over thirty samples were collected with tenax/carboxen 569 (a Supelco product consisting of carbonized molecular sieve) adsorbent tubes at flowrates of 80 cc/min for representative sample periods. Samples were collected during normal administrative work hours, as well as during the evening training sessions involving live burns within mock-up structures. Analysis was by GC/MS for volatile organic compounds including a library search for non-target compounds, using EPA Methods T01 and T02 (2).

Temperature and pressure measurements were made using temperature probes, an inclined manometer and magnahelic gauges. Observations were made of the potential effects of barometric pressure on possible gas movement. Significant changes in well pressure difference may suggest the occurrence of a chimney effect in the mockups during burns, potentially causing gas migration from the ground into the mockups.

RESULTS

Results indicated that, while there was evidence of VOCs in ambient air at the site, the concentrations found were in the low ppb range, and were not considered an immediate threat to site personnel. Table 1 summarizes the maximum values detected. The compounds detected in the air were similar to those found in soil and ground water on the site and some are typical of landfill gas. There is often difficulty in assessing the results in regard to appropriate safe levels for VOCs especially for samples of indoor air (3). The levels found were below IDLH levels, OSHA PELs, and ACGIH TLVs. However, given the presence of subsurface gas and the potential controlling effect of the landfill gas extraction systems, there is potential for air quality deterioration. Some of the highest values of VOCs were detected in the maintenance garage.

Sampling in the mockups during the live burns with adsorbent tubes was limited due to the harsh environment (high temperatures, water, heavy smoke and combustion products) within the mockups during live burns. Low (generally less than 10 ppb) concentrations of seven VOCs were detected at this location.

Differential pressure measurements in gas monitoring wells near the mockups during fire training exercises showed no significant variability attributable to fire training activities involving live burns. A pressure gradient was detected from measurements in gas monitoring wells with greater negative pressures near the landfill boundary and lower negative pressures measured near the mockups, due to the influence of the landfill gas extraction systems. The landfill gas extraction systems were likely influencing movement of subsurface gases at least as far from the landfill as the mockup buildings, as indicated by negative pressure measurements in wells near the mockups during normal operations (i.e., when live burn exercises were not ongoing).

DISCUSSION

Under normal conditions, measured VOC levels were generally low, but results were obtained from only a few discrete periods, when the landfill gas extraction systems were operating. Periodic air sampling was recommended to observe any changes in contaminant concentrations over time (i.e., months, years).

The landfill gas control systems were shown to exert subsurface influence on the site at least as far as the mockup buildings, likely controlling vapors on the site (via the subsurface). Increased concentrations of gases could result if the landfill gas control systems failed or were operated with reduced effectiveness. Some of the risks involving this situation are attributed to the uncertainties associated with variations in system performance on gas and vapor migration patterns, atmospheric pressure effects and also on what effect duration of upsets would have on the gas migration.

RECOMMENDATIONS

The greatest risk appeared to be associated with the uncertainties and possible variability in the effectiveness of the landfill gas control systems, it was recommended that air monitoring be performed along the perimeter of the site and at some specific locations onsite.

An automated detection system was recommended for this consisting of remote sensors installed at key locations, a central display and recording system to provide easy and continual identification of the status of hazard conditions, and warning devices (alarms/lights) to alert personnel of potentially hazardous conditions. The primary constituent to monitor would be combustible gas. The output of the monitoring system would be used to curtail or restrict activities in parts of the site or suspend operations until the alarm condition subsides and/or the cause identified and the hazard evaluated.

The results from the monitoring system may be used to curtail or restrict activities in parts of the site or suspend operations until the alarm condition subsides and/or the cause identified and the hazard addressed.

In addition to monitoring, the following procedures (some of which had already been implemented) were recommended to minimize potential risks:

- Check mockup buildings for combustible gas and organic vapors before and during any maintenance work, especially any welding or similar activity. Suspend work if measurements exceed prescribed action levels;

- Vent mockups when not specifically in use for fire training and during maintenance and recharging activities;

- Monitor wind direction/speed with a fixed system with recording devices for historical record and also with wind socks at various locations visible from different areas of the site;

- Encourage use of communications systems (i.e., radios) for personnel working on different parts of the site;

- Encourage reporting and documentation of monitoring and the occurrence of unusual events (ie accidents, incidents, fires, odors, gases, etc.)

- Establish a safety organization to address safety issues of site contamination and enforce the operational safety plan which was developed based upon the findings of this study.

CONCLUSIONS

The study involved unusual site conditions, diverse concerns requiring a monitoring program that was planned and designed, to address the major concerns; and to provide recommendations for mitigation and monitoring. Since immediate hazards were not detected the resultant concern was for potential hazards due to changes in the situation associated with the landfill gas extraction systems; therefore the primary recommendation was to continue monitoring for indicator parameters that would provide an early warning of changes in the onsite gas situation.

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Table 1 SUMMARY OF MAXIMUM CONCENTRATIONS MEASURED

COMPOUND	MAX CONCENTRATION (PPB)
ACETONE	63.3
ACRYLONITRILE	18.7
BENZENE	48.1
2-BUTANONE	57.2
CARBON DISULFIDE	4.3
CHLOROBENZENE	0.9
CHLOROFORM	1.6
CHLOROMETHANE	47.4
1,2-DICHLOROETHENE	5.2
ETHYLBENZENE	28.4
2-HEXANONE	638.1
4-METHYLPENTANONE	66.8
METHYLENE CHLORIDE	12.3
STYRENE	86.1
1,1,2,2-TETRACHLOROETHANE	4.6
TETRACHLOROETHENE	5.3
TOLUENE	139.0
1,1,1-TRICHLOROETHANE	45.1
TRICHLOROETHENE	12.9
XYLENES	289.6

Traverse-Monitoring for Superfund Sites

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Awareness is increasing that activities related to the clean-up of Superfund sites can lead to air emissions having significant effects off-site. Because these emissions are often unplanned or temporary, project managers are frequently reluctant to dedicate resources to what is thought to be an unlikely public health concern. Without further information fitting the monitored concentrations into the structure of the plume, a single monitor at fence-line is, in most cases, inadequate. A single measurement of concentration, without an understanding of where it resides in the plume distribution, does not enable an adequate estimation of downwind dilution.

This paper introduces an inexpensive technique-- entailing the use of hand-held monitors, on-site wind data, and *a priori* modeling and toxicological analyses-- which enables on-site personnel to make informed decisions concerning evacuation and other potential response to ground-level emissions from Superfund sites. Additionally, a method of bridging the gap between information and decision-making is offered.

While the techniques offered in this paper may be used to fulfill EPA policy, they are presented here for informational purposes only. This paper is not to be construed as official EPA policy or guidance. Mention of brand-names in no way constitutes endorsement.

INTRODUCTION

Activities related to the remediation of Superfund sites can lead to air emissions having significant impact off-site. During the Fall of 1989, the authors of this paper were asked to develop a contingency plan as part of an effort to protect public health in case of accidental chemical spills during remediation activities at the Maryland Sand, Gravel, and Stone Superfund site. This paper describes a technique enabling on-site personnel to make informed judgments concerning evacuation and other response to an accidental spill of volatile organic chemicals. Not surprisingly, the crux of this plan involves quantifying, in a timely and accurate manner, the parameters important to decision-making. This is accomplished by performing as much *a priori* analysis as possible and delineating straightforward procedures for the gathering of necessary information. The technique developed for Maryland Sand included two novel concepts: the integration of modeling with traverse-monitoring to assess impacts, and the development of Response Indices explicitly linking decision-making with data collection and analyses.

Specifications

To be useful, the technique must (1) enable decision-making to be based on estimates of risk that are neither overly conservative nor non-conservative; (2) provide real-time information; (3) not represent an undue hardship to the potentially responsible party in terms of resource requirements. The

development of this technique can be divided into two tasks. First, it is necessary to determine what decision needs to be made and what criteria are to be used to make it (action levels). This requires the identification of information that will be important in the decision-making process before the procedures for gathering this information can be developed. The second task is the development of a means of data collection and analysis to supply the needed information.

Bases for Decision-Making

Three factors were quickly identified as directly impacting decision-making: pollutant concentration at *sensitive receptors* (as opposed to an arbitrary point along the fence line), chemical-specific toxicity, and duration of exposure.

The next step was to bridge the gap between data collection/analysis and on-site decision-making. This was established by developing new quantities called Response Indices. We developed these indices to employ toxicological and atmospheric analyses to relate measurable on-site phenomena with proper responses. Each of the Response Indices was a function of factors identified above such that

$$RI = f(\text{contaminant concentration, toxicity, duration}).$$

Next, we developed methods of data collection and analysis to quantify each parameter.

DATA COLLECTION AND ANALYSIS

Estimating Concentrations at Downwind Receptors

Before the traverse-monitoring method was developed, on-site monitoring and modeling were considered for use in estimating impacts. It was soon apparent that these techniques were, for various reasons, insufficient. Brief descriptions of these alternatives are offered below.

On-site Monitoring

It is common practice to place a monitor or two at the fence line of a site with the expectation that off-site impacts will be quantified. While a monitor can offer reliable, real-time information concerning pollutant concentrations at a single place and time, this information alone, without fitting the monitored concentration into the structure of the plume, is inadequate to quantify impacts elsewhere. (This is true even for the ground-level sources under consideration here.) Figure 1 shows three instances in which a monitor at the fence line of a site would record identical concentrations, even though impacts off-site are quite different for each case. Without knowledge of the source-strength, the width of the plume, and where the monitored concentration fits within the concentration distribution of the plume, downwind impacts may be underestimated.

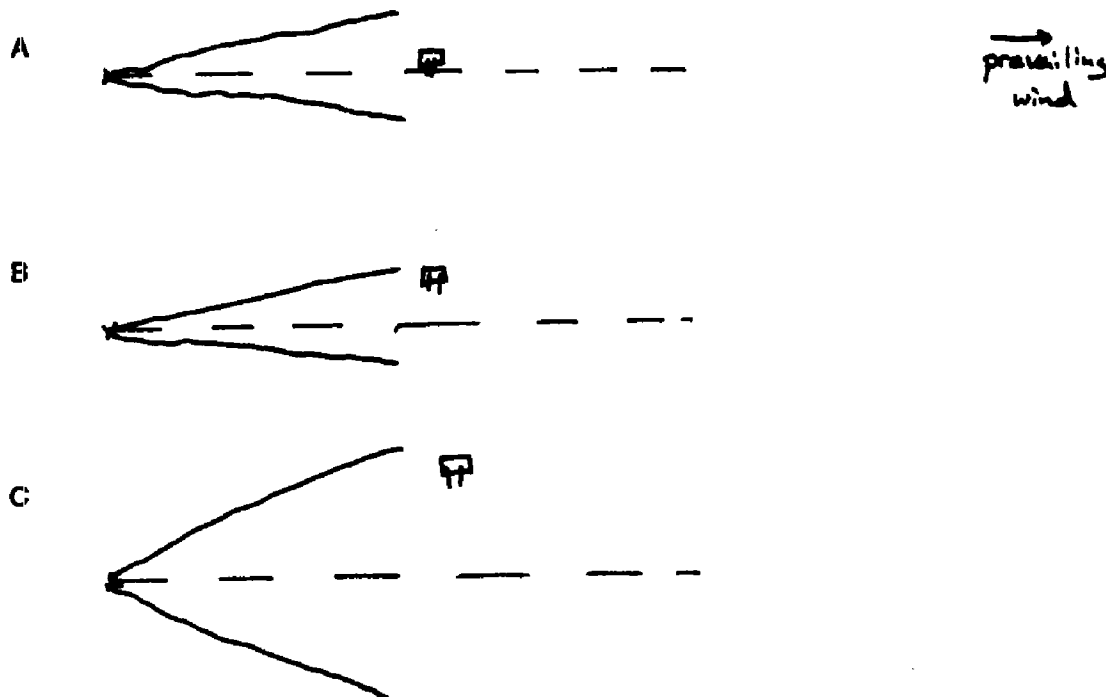
Modeling

Air dispersion modeling can often provide information that monitoring cannot. Unlike a single monitor, a model applies theoretical and empirical knowledge of how pollutants are transported and diffused through the air to estimate impacts. Additionally, models are quite able to predict the maximum impacts that can be expected from a given source of emissions. Monitors cannot make predictions, especially of the maxima that are relevant for most regulatory purposes.

For the present application, however, modeling has several drawbacks. First, modeling requires both source and site specific information: One must characterize the source (emission rate, size, and location relative to receptors) and the atmosphere (wind speed and direction and atmospheric stability). These requirements make (near) real-time estimates of impact impossible without collecting real-time

meteorological data. Second, in the event of accident, such as the rupturing of a drum with unknown contents, the source strength will be unknown, making the estimation of impacts impossible. Finally, the screening procedures that are often used to simplify modeling exercises are not applicable to this case. Over-conservatism is likely to induce overreaction, including needless evacuation, and the invoking of unwarranted measures may not only cause unnecessary inconvenience and trauma, but also diminish the sense of urgency and when, actual emergencies develop.

Figure 1



This figure describes three very different situations when a single monitor at fence-line would show the same impacts, showing that downwind impacts cannot be predicted with a single, stationary monitor. In this case, emissions from source A are less than those from source B, which are, in turn, less than those from source C.

Traverse-Monitoring

The traverse monitoring technique is a marriage of monitoring and modeling developed to exploit the strengths of both methods. It is based upon the incorporation of data reported by a technician who walks through the plume while carrying a hand-held VOC monitor. The smooth, Gaussian distribution that is often used to characterize the distribution of a pollutant within a plume exists only as a result of the time-averaging of many instantaneous pictures; each of which would be characterized by some maximum concentration $x_{\text{max},i}$. As a rule, $x_{\text{max},i}$ is greater than x_{avgmax} , the time-averaged maximum found along the time-averaged centerline (that is, the average of maxima unpaired in space); thus $x_{\text{max},i}$ can be used to develop conservative estimations of x_{avgmax} . Quasi-instantaneous maxima can be measured by traversing the me with an Hnu meter or some other device capable of continuous or near continuous reports of total VOC concentrations (with very short lag time). In this way, concentrations can be monitored at a known relative position within the me.

The time-averaged maximum can then be approximated as follows:

$$x_{\text{avgmax}} = \frac{1}{n} \sum_{i=1}^n x_{\text{max},i} \quad (1)$$

where: n = the current traverse number (e.g., 50 for the 50th traverse)

N = the number of traverses to be averaged

$$i = n - N$$

$x_{\max,i}$ = instantaneous maximum concentration in the
me at the downwind distance of the traverse
(real-time, on-site measurement).

Thus, x_{avgmax} is updated with each traverse, and the variable n behaves much like a dimensionless time. There are two factors to be weighed in the selection of an appropriate N . First is response-time toxicology (What time-frame is important with respect to the chemicals present and the protection of health, and how much time is necessary to take corrective action? This method is inappropriate where "single-breath" concentrations are important). Second is the level of stability required. (The instantaneous maximum will vary significantly with each traverse; the more traverses that this "running average" encompasses, the less sensitive it will be to fleeting fluctuations which could induce overreaction.) Clearly, the role of the toxicologist is important in selecting a suitable N .

The following procedure was recommended for the Maryland Sand, Gravel, and Stone site:

At the commencement of the incident the person who is to perform the traverses will note the average flow vector of the wind (the direction toward which the wind is blowing) and position himself 100 meters directly downwind; he will then walk 50 meters in a cross-wind direction (That is, if he positioned himself by starting at the source of emissions and walking 100 meters downwind, he will now turn 90 degrees to his right or left and walk for 50 meters). Now he is ready to traverse the plume. Each traverse consists of a 100 meter walk (at a deliberate pace) perpendicular to the wind direction and beginning and ending 50 meters from the plume centerline. During each traverse, the traverser will monitor his Hnu meter and report the maximum observed concentration (in ppmv). The time-averaged, centerline concentration is then approximated as in Equation (1) letting N , in this case, equal 10.

Once the centerline concentration at a known distance is estimated, a Dilution Factor, D , can be used to estimate concentrations farther downwind. D is a function of wind speed, stability and distance from the source. The Dilution Factor can be estimated using standard air diffusion models by predicting centerline concentration near the traverses and at the point of interest downwind. The Dilution Factor is the ratio of these predictions such that

$$x_R = D * x_{\text{avgmax}} \quad (2)$$

where x_R is the concentration at the receptor of interest.

The Dilution Factor is estimated as a function of atmospheric stability category and wind direction (the wind direction dictates if the me will travel in the direction of a nearby home or a distant one; the locations of sensitive receptors are built into the Dilution Factors, which are direction-specific). The stability category can be inferred from lateral turbulence in the atmosphere (EPA, 1986) which, along with wind direction, will be measured on-site. For the case of Maryland Sand, Dilution Factors were calculated and tabulated for use on-site.

Time-Frame

Time-dependency is incorporated into decision-making in two ways-- through the selection N (number of traverses to be averaged) and through a *a priori* period-of-exceedence minimums attached to the Response Index (e.g. "If the RI remains greater than 1.0 for 20 minutes, then initiate emergency measures").

Toxicology

The Toxicological Factor, T , relates the concentrations of individual VOCs at the downwind receptor to the Response Index, and must be defined in such a way as to make RI understandable and useful. Essentially, T encompasses the important toxicological information, such as chemical composition and exposure limits, that is necessary to evaluate the significance of concentrations of total VOCs predicted using the Dilution Factor. The units used to describe T should be the inverse of those used to describe x_R so that the Response Indices will be dimensionless.

For our application, T was developed as a function of chemical composition and tolerance limits only, and we use an additive response approach to define the Toxicological Factor for each chemical as the ratio of its mole fraction (as a proportion of all VOCs) and its tolerance level and has units of ppmv⁻¹. The overall T is the sum of these ratios:

$$T = \sum_{i=1}^x (\text{mole fraction} / \text{tolerance}) \text{ over all chemicals} \quad (3)$$

where x = the number of chemicals detected

Tolerance levels and molecular weights for chemicals suspected to be on-site were tabulated for use on-site.

Mole fractions must be measured on-site with a gas chromatograph analyzer or similar machine. Integrated, 5-minute bag sampling for GC analyses can be performed directly downwind of the source. GC analyses are performed after the first few instantaneous maxima have been found by traversal and, subsequently, every 30 minutes using a portable GC (Qualitative analyses are updated periodically due to the non-uniform rate of volatilization of VOCs).

THE RESPONSE INDICES

We are now in a position to quantitatively define the Response Indices as follows.

$$RI_i = x_{\max,i} * D * T \quad (4)$$

$$RI_n = x_{\text{avgmax}} * D * T \quad (5)$$

where: $x_{\max,i}$ = instantaneous, maximum concentration across the me at a prescribed downwind distance (from real-time, on-site measurements).

x_{avgmax} = time-averaged centerline total contaminant concentration at a prescribed distance (concentration estimated from real-time, on-site measurements).

D = Dilution Factor which relates x_{avgmax} to concentrations of the pollutant at sensitive receptors farther downwind (x_R), s.t. $x_R = D * x_{\text{avgmax}}$.

T = Toxicological Factor which relates estimated concentrations of individual contaminants at receptors to the Response Index, s.t. $RI_i = T * x_R$.

Note that the Response Index is "self-normalized" to 1.0 through the assumption of additive response toxicology.

By substituting Equations (1) and (5) into equation (4) above we obtain the time-averaged Response Index

$$RI_n = \frac{1}{N} \sum_{i=n-N}^n (RI_i) \quad (6).$$

Through the Response Indices, RI_n and RI_i , we may relate events on-site to predetermined, thoroughly considered responses. For the Maryland Sand site, the following protocol was used.

Traverses will commence if, at any time, a total VOC concentration of 20 ppmv is measured in the pit. If no VOCs are detectable by the traverser in 30 minutes, then traversals may be discontinued. If RI_i is not increasing then traversals may cease if (a) RI_i fails to exceed 1.0 within the first 30-minutes, or (b) if RI_i fails to exceed 1.0 in any subsequent hour. However, traversals may never be discontinued if RI_i is increasing.

CONCLUSIONS

The development of Response Indices to bridge the gap between data collection/analysis and decision-making is inherently flexible; the parameters can be weighted or entirely different parameters can be used. A Response Index approach can be helpful in almost any situation that is too complicated for intuition or common sense or simple guidelines to rule. The exercise of developing Response Indices has great merit in itself: it forces the explicit examination of the problem for parameters of importance.

The traverse-monitoring technique has wide applicability and can be used in most situations where an unknown quantity of volatile organics are emitted from a small, ground-level source. As noted above, this technique is not applicable in cases where single-breath doses are of concern.

At this juncture, the traverse monitoring technique can benefit from development in two areas. One is automating the process of manipulating the several sets of data that are necessary to calculate the Response Index during each traverse. This would consist of a computer program that incorporates the *a priori* modeling and toxicological analysis with the data that are collected on-site. A second means of improvement is a field study to estimate the difference between the monitored center-line concentration and that which would be estimated using conventional modeling techniques.

Although the traverse monitoring technique has only been employed at the Maryland Sand site, it could potentially gain great popularity as a convenient, inexpensive method of quantifying off-site impacts from uncontrolled emissions of volatile organics.

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**THE U.S. AND CALIFORNIA
CLEAN AIR ACTS: IMPLICATIONS FOR THE FUTURE**

By John T. Ronan III
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The "Decade of the Environment" will bring with it stringent environmental controls and pervasive regulation affecting most areas of the national economy.

All of the "easy" technical solutions for environmental control have been used to meet current environmental laws. Future controls must necessarily involve restrictions on manufacturing, transportation and the consumption of energy. Stringent environmental regulation of the 1990's will therefore impact upon the economy, personal lifestyle and politics.

The environmental controls of the 1990's will create a collision between economic costs, political realities and environmental benefits. Much of the regulatory activity in the 1990's will involve the resolution of this conflict.

Federal Clean Air Act Amendments of 1990

Key Provisions

Title 1 - Attainment and Maintenance of Ambient Air Quality Standards

Non-attainment areas rated Moderate to Extreme. Most areas are to achieve federal standards by the year 2000 and the six worst areas by no later than 2010.

Title II - Mobile Sources

Stringent controls on automobiles and other vehicles. Mandatory use of methanol/ethanol fuels for the worst non-attainment areas.

Title III - Air Toxics

Stringent controls upon manufacturing plants emitting air toxics with regulation based upon risk assessment. Noncompliance will result in forced plant closures.

Title IV - Acid Deposition Control

Stringent acid rain controls directed towards 50% reduction in nationwide sulfur dioxide emissions, with a heavy impact upon Mid-western electric power generation.

Some 101 cities have failed to meet the 1987 deadline for the ambient air quality standard for ozone, the main constituent of urban smog.

Compliance Deadlines for Non-Attainment Areas:

2010 - Extreme Area (Los Angeles)

2005 - Severe Areas (San Diego, Chicago, Houston, New York, Philadelphia)

2000 - Serious Areas (Washington, D.C., Boston, Atlanta, Sacramento, Fresno and 30 other cities)

1995 - Moderate (San Francisco Bay, Santa Barbara and 60 other cities)

Increments of progress:

Initially 4% annual reductions in non-attainment pollutants.

Later 3% annual reductions until standards achieved.

In severe and extreme areas, additional reductions in smog-forming chemicals (reactive volatile organics) from plants emitting over 50 tons a year.

Bus fleets in urban areas to run on natural gas. Car pool, parking and other transportation restrictions and controls.

Economic Impacts

Annual Costs

Total cost \$21 to \$30 billion annually.

Urban Smog Reduction

Total cost from \$11.5 to \$20.5 billion annually including \$3.0 to \$12.0 billion for cleaner automobiles and cleaner fuel.

\$2.5 billion for emission reduction from landfills, dry cleaners, chemical plants and stationary sources.

\$1.0 billion in local enforcement programs.

\$5.0 billion for state programs.

Air Toxics Reduction

At least \$5.5 billion and probably greater depending upon implementing regulations to be promulgated in the future.

Acid Rain Reduction

\$4.0 billion for electric utilities to install scrubbers, to convert facilities and to purchase low sulfur coal.

California Clean Air Act of 1988

Substantially more stringent than Federal Clean Air Act Amendments.

Smog-related controls relating to reactive volatile organics.

Transportation controls.

Consumer products regulation and restrictions.

District wide emissions shall be reduced 5% or more a year for each non-attainment pollutant or its precursor (averaged every three-year period) until federal standards are achieved.

Non-Attainment Districts Are Classified As

Moderate Air Pollution - Attainment of federal standards by December 31, 1994.

Serious Air Pollution - Attainment of federal standards by December 31, 1997.

Severe Air Pollution - (Los Angeles) Reduction of ambient pollution levels by 25% by December 31, 1994. Reduction by 40% by December 31, 1997. Reduction by 50% by December 31, 2000, based upon the average base line of 1986 through 1988.

Stringent regulation will be imposed upon Districts which though listed as Moderate, contribute to pollution in other Districts through air transport of pollutants. (Example, San Francisco Bay Area.) A District attainment plan will include allowances for pollution transport both upwind and downwind of the District.

Hayden-Van de Kamp Initiative on November 6, 1990 Ballot

Greenhouse Gas Reduction Plan "to reduce annual emissions of any gases which may contribute to global warming" (in the judgment of the Air Resources Board). Maximum feasible reductions are to be achieved, with a mandatory reduction of 20% by January 1, 2000, and 40% by January 1, 2010, based upon 1988 levels. These percentages are to be adjusted to reflect any difference between the projected rate of population growth in California and that of the United States.

Greenhouse gases include carbon dioxide, chlorofluorocarbons, halons, nitrogen oxide, methane and any other gases so designated by the State. Gases are to be controlled in proportion to their respective contributions to global warming.

Imported electric power generated out-of-state will be curtailed to the extent that these generating plants contribute to global warming.

Products whose manufacture contribute to global warming will be banned and their import into the state prohibited.

The Greenhouse Gas Reduction Plan would be the most important economic event in California since the "energy crises" in 1979. Energy prices would increase by \$10 to \$15 billion annually by the year 2000, based upon California Energy Commission assumptions. California would be able to support one million fewer jobs by the year 2000, principally in the manufacturing and construction areas. Annual energy prices are estimated to increase from \$25 to \$45 billion by the year 2010.

Economic Costs of National Greenhouse Gas Controls

The following economic projections are based upon economic models by Alan Manne, Stanford University, and Richard Richels of the Electric Power Research Institute. The model is based upon the limitation of carbon dioxide emission to 1990 levels through 2000 and then the gradual reduction to 20% by 2030.

Assuming no replacement technology, the annual cost would reach \$500 billion. If replacement technology were available, the annual cost would be \$50 billion.

Cumulative Costs through 2100 (present value),
Manne-Richels Model

Scenario I - Pessimistic . . . \$3.6 Trillion

No practical way to shift to clean energy technologies;
no automatic increase in economic-wide energy efficiency.

Scenario II - Moderate . . . \$1.8 Trillion

Automatic energy-efficient adjustment of one percent per
year.

Scenario III - Optimistic . . . \$800 Billion

Cost effective substitutes for fossil fuel energy
available; one percent energy efficient adjustment per year.

Conclusions

Clean Air legislation in the 1990's will have a major
impact on the national and state economies, politics, and
personal standards of living.

Existing control technology has been utilized to the
extent available to meet current standards. Future standards
must be met largely by curtailment and restrictions. Future
Clean Air legislation will mandate public and private
transportation controls. Clean Air Act legislation will
reach as far as consumer product regulation. Even if new
technology can be developed, the deadlines imposed by pending
legislation may be too short for adequate new technology to
be developed.

If Greenhouse gas reduction legislation is adopted, a
reduction in energy consumption will be mandated as nuclear
power is currently a politically unacceptable alternative.
Depending upon the degree of regulation, Clean Air Act
regulation could range from costly to recessionary in its
economic impact.

As the government implementation of Clean Air Act
legislation evolves, conflicts and tradeoffs will necessarily
require a resolution between economics, politics, and
environmental benefits. The 1990's, the "Decade of the
Environment," will therefore involve difficult and costly
decisions as we confront the reality and the costs of
environmental control.

SUPERFUND COMMUNITY RELATIONS PLANS: TAKING ADVANTAGE OF THE REQUIREMENT

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Community Relations Plans are now treated as serious components of Superfund site activities. Community relations planning can be approached in two ways: grudgingly, in conformance with minimal agency requirements, or proactively, with long-term project goals in mind. When Community Relations Plans (CRPs) are used to encourage the participation of concerned parties in the early stages of remedial action planning, time and money may be saved during the later stages of the project approval process.

This paper will make the case for taking advantage of the requirement and undertaking a proactive approach to community relations planning. It will describe the regulatory basis and the implementation requirements of Community Relations Plans. Conclusions will be drawn as to how effective community relations planning can contribute to the favorable resolution of Superfund projects.

Introduction

In 1980, Congress enacted the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), the landmark legislation now known as "Superfund". Superfund responded to the American public's growing perception that not enough had been done to manage the public health and safety implications of toxic and hazardous waste dumping.

Two years earlier, extensive media coverage had exposed people in communities all over the country to the environmental and human tragedy of unrestricted toxic dumping at the Love Canal site in New York. Television broadcasts showed public officials who seemed powerless as industry spokespeople sought to avoid responsibility for this disaster. Voters clamored for redress. By enacting CERCLA/Superfund, Congress gave the Environmental Protection Agency (EPA) authority to assign responsibility and exact payment for the clean-up of contaminated toxic and hazardous waste dump sites. Superfund overturned years of "business as usual" practices for both industry and the agencies suddenly charged with implementing Superfund.

The finer points of Superfund enforcement are still being resolved. The legislation was interpreted by the National Oil and Hazardous Substances Pollution Control Contingency Plan (NCP) of 1982, which defines and authorizes enforcement and implementation responsibilities. The Superfund Amendments and Reauthorization Act (SARA) of 1986 set forth additional requirements and guidelines. The practical implementation of Superfund has also been refined through time and experience.

The Superfund study process comprises several formally defined phases: the Remedial Investigation/Feasibility Study (RI/FS), the Remedial Action Plan (RAP), and Remedial Design/Remedial Action (RD/RA). Community Relations Plans (CRPs) are designed to be implemented concurrent to these phases of Superfund activities.

Interim handbooks detailing guidelines for the implementation of CRPs were issued in March and June, 1988, by the EPA's Office of Emergency and Remedial Response. The June, 1988, handbook, entitled "Community Relations in Superfund", currently serves as the agency's formal guidance document.

Since the first interim handbook was published in 1988, Federal and State Superfund enforcement agencies have expanded the requirements for preparation and implementation of formal, extensive CRPs as part of most Superfund projects. CRPs are a logical vehicle for addressing the increased sophistication and expectations of the public regarding Superfund projects and toxic contamination issues.

Objectives and Implementation Requirements

Objectives

The Superfund community relations effort promotes communications between the public, potentially responsible parties ("PRPs" - site owners and others who may be responsible for clean-up costs), and the lead government agency responsible for Superfund enforcement actions.

EPA's current handbook (June, 1988) on CRP implementation lists the overall objectives of community relations as follows:

- **Give the public the opportunity to comment on and provide input to technical decisions.** An ongoing community relations effort should encourage and assist the local public to contribute to agency decisions that will have long-term effects on their community.
- **Inform the public of planned or ongoing actions.** Community relations activities should inform the local public of the nature of the environmental problem, the threat it may pose, the responses under consideration, and the progress being made.
- **Focus and resolve conflict.** Conflict may be unavoidable in some circumstances, but it can be constructive if it brings into the open alternative viewpoints based on sound reasons for criticism or dissent. An effective community relations effort channels conflict into a forum where it can serve a useful purpose.

EPA has identified two ways in which its ability to make useful decisions can be enhanced by public input:

1. Communities are able to provide valuable information on local history, citizen involvement, and site conditions; and
2. Identifying the public's concerns enables EPA to fashion a response that is more responsive to community needs.

The concerned community often maintains its own set of community relations objectives. These might include:

- to be included in decisions that impact the community; and
- to influence decision-making by regulatory agencies and PRPs so that final Remedial Action Plans safeguard the health and safety of community members, and protect property values and quality of life.

Site owners and others who may be financially responsible for remedial action often enter the CRP process with objectives that are very different from the community's. Remedial action alternatives can vary drastically in terms of cost in time and money, and responsible parties can have thousands or millions of dollars at stake. Site owners and PRPs may fear the CRP process as cumbersome at best; at worst, the dissemination of "scary" technical information to a comparatively uninformed public may seem a risk fraught with dangers to the bottom line. Therefore, PRPs might conclude that the best objective is to avoid the community relations gauntlet by minimizing contributions to the process.

It is the contention of this paper that the proactive, effective use of the CRP process should not increase financial risk or liability to site owners and PRPs; rather, it should serve as an opportunity to manage that risk. This issue will be discussed in further detail in the CONCLUSIONS section.

Consultants and community relations specialists are often retained to manage the CRP process for site owners and PRPs. As their client's representatives, these consultants must necessarily focus on their client's objectives. Given that participation in the CRP process is mandated by law, some consultants would advise their clients to take advantage of the requirement by adopting the following objectives:

- communicate effectively with the interested community so that upset and controversy can be avoided;
- coordinate effectively with regulatory agencies so that delays, revisions of documents, etc., can be minimized; and
- generate community and regulatory agency support for a preferred remedial action alternative.

PRPs should recognize the potential value of a process that can be used proactively to influence the selection of a remedial action alternative.

Implementation Requirements

In overview, EPA's CRP implementation requirements follow this schedule of key tasks:

1. Conduct community interviews.
2. Prepare the Community Relations Plan (CRP).
3. Establish locations for information repositories and administrative records.
4. Complete the Remedial Investigation/Feasibility Study (RI/FS) and proposed Remedial Action Plan (RAP).

5. Provide for public comment and the opportunity for a public meeting on the proposed RAP.
6. Prepare a responsiveness summary of significant public comments on the RI/FS and the RAP.
7. Prepare an explanation of any differences between the Final RAP and other actions taken.
8. Provide for public notice of the selection of the remedial action alternative.
9. Revise the CRP, if necessary, to provide for community concerns regarding remedial design/remedial action (RD/RA).
10. Prepare a fact sheet for the public explaining final engineering design.

The CRP should include a description of the site background, history of community involvement at the site, community relations strategies, a schedule of community relations activities, and a list of affected and interested groups and individuals. EPA recognizes that details of the CRP process will vary in response to the unique conditions of each project.

Conclusions - How to Make Community Relations Plans Work

In a society that is increasingly centered on information exchange, the best long-term strategy for business, government and the public is to promote the exchange of information that is accurate, relevant and complete. The CRP process is most effective when:

- communication is clear and frequent between all concerned parties: PRPs, regulatory agencies, the community and any consultants who may be involved;
- the PRPs (and consultants) take a proactive approach by identifying and contacting community leaders/public interest groups early in the process and presenting information in a way that is meaningful to the audience;
- the regulatory agencies provide consistent direction and timely review of documents; and
- the community reads and understands pertinent technical information so that comments and questions are germane and appropriate.

When CRPs are used to encourage the participation of concerned parties in the early stages of remedial action planning, time and money may be saved during the later stages of the approval process. Early public input to remedial action planning provides for the development of documents that will "fly" and minimizes the need for costly revisions and delays.

CRPs give the public a say in actions that may impact its future. Conversely, CRPs provide a forum that allows PRPs to present their perspectives and make the case for preferred alternatives and project resolutions. For example, discussions during early stages of the CRP process might lead to public support for a less costly on-site remediation alternative, should this alternative reduce risk that might result from transportation of hazardous materials or should this alternative allow for more timely remediation and re-use of the site.

The CRP process enables PRPs to explain why a publicly supported alternative may be prohibitively expensive or otherwise unworkable, and it allows the public to clarify priorities and ensure that key concerns are addressed. CRPs create additional work for implementing agencies, but they can also shorten and simplify the RAP and RD/RA processes by managing controversy and building compromise.

Community Relations Plans are a natural response to the times. Given that the public is no longer conditioned to accept the conclusions of site owners and regulators on faith, CRPs provide a mechanism that allows both PRPs and the community to work with regulators and contribute to remedial action planning so that compromises leading to ultimate project resolution can be reached. In conclusion, the community relations process can and should be used to develop workable, viable Superfund Remedial Action Plans that will result in better environments for all of us.

THE EVALUATION OF BREATH VOCs RESULTING FROM
HUMAN EXPOSURE TO MICROENVIRONMENTS

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Abstract

Breath measurements offer the potential for a direct and noninvasive evaluation of human exposure to volatile organic compounds (VOCs) in the environments in which people live and work. This research study was conducted to further develop the potential of this exposure assessment methodology. Air samples were collected in 32 microenvironments to determine a few possible sources of human exposure to selected VOCs. Several people were exposed to the atmosphere in six microenvironments for several hours. Air concentrations of VOCs were measured during these exposures and breath samples were collected and analyzed at multiple time points after the exposure to evaluate elimination kinetics. Elimination half-lives were estimated using mono- and biexponential pharmacokinetic models. Analysis of microenvironment air samples from homes, workplaces, vehicles, etc., revealed a wide range of potential human exposures to VOCs at concentrations from 1 to 16000 $\mu\text{g}/\text{m}^3$. In general, a biexponential function provided a better fit to the decay data than did the monoexponential function. One-compartment half-lives ranged from 0.08 h for n-nonane to 4.3 h for 1,1,1-trichloroethylene. Two-compartment half-lives ranged from 0.03 h for m,p-xylene to 0.78 h for one dichloromethane measurement for the first half-life, and from 0.61 h (n-octane) to 21 h (p-dichlorobenzene) for the second half-life.

Introduction

During the past decade, the U.S. EPA has conducted studies designed to assess personal exposure to volatile organic compounds (VOCs) through its Total Exposure Assessment Methodology (TEAM) program. In addition to indoor and outdoor air samples, samples of exhaled breath were also collected^{1,2} and statistically significant correlations were observed between breath concentrations of specific chemicals and a person's activity or presence in a distinct microenvironment³. Microenvironments are defined as discrete locations where people live, work, or visit with distinct sets of activities or characteristics that effect VOC emissions and airborne concentrations. Consequently, two general questions have arisen: (1) what are the common personal activities and microenvironments that may lead to elevated human exposure to VOCs and (2) can breath measurements provide a quantitative measure of VOC exposure?

The analysis of breath for VOCs has a number of advantages over the use of personal (exposure air) monitoring. First, the collection method is simple and can be completed in approximately one minute. Thus the burden associated with the collection of a breath sample is less than that of a personal air sample. It can also provide a noninvasive alternative to blood collection and analysis methods in the estimation of body burden. The presence of the VOC in breath serves as a biological marker of exposure and is more reflective of dose than is an exposure air measurement. If the uptake and elimination characteristics of the VOC by the body are understood, the possibility exists that breath measurements made at a known time after the exposure can provide an estimate of the exposure (air) concentration. Although breath excretion rates of a few VOCs have been measured in a few subjects⁴, further information is needed for more compounds, subjects, and exposure levels for the development of accurate predictive models.

The purpose of this study was to evaluate some common personal activities and microenvironments that might lead to elevated VOC exposures, and to determine the breath VOC concentrations that result from exposure, including low level exposure, to a variety of chemicals. We also wished to test a new breath sampling device and to use it, whenever possible, to follow the decay of VOCs from the body and to calculate pharmacokinetic parameters, such as the elimination half-lives, that can be used for the development of exposure-prediction models.

Experimental Methods

Air, Breath Sampling and Analysis

Most of the air and breath samples described in this manuscript were collected into evacuated SUMMA polished stainless steel canisters fitted with a shutoff valve. For screening of the microenvironments, "grab" samples of air were collected in most locations by opening the canister for approximately one minute without a flow restricting orifice. Longer-term integrated samples (restricted inlet) were collected in some cases when the VOC emissions were unpredictably time dependent. In some cases, the analyses of less volatile organic compounds were facilitated through the retention of the chemicals on a Tenax-GC sorbent bed as a known volume of air was passed through the system⁵. The VOCs in exhaled breath samples were collected onto Tenax-GC⁶ or into canisters from either a Tedlar bag⁷ or a new, miniaturized spirometer⁸ capable of collecting the breath sample in approximately one minute. The Tedlar bag spirometer collected whole breath

and the miniaturized spirometer collected predominantly alveolar air⁸. Their side-by-side use here was an aspect in the development of the miniaturized device⁹.

Analysis of VOCs from canister samples (air and breath) was conducted using a gas chromatograph/mass spectrometer (GC/MS) with a cryofocussing trap similar to that of McClenny⁸ and completely described elsewhere¹⁰. In general, the analysis of canister samples for polar analytes was not performed because of the losses associated with the water-permeable Nafion membrane in the inlet system. The removal of water from breath samples was found to be necessary in order to prevent freezing of the cryogenic trap. Adsorbed VOCs were recovered from Tenax-GC via thermal desorption. The released vapors were focussed onto a cryogenically cooled trap (-196°C) with subsequent introduction in a GC/MS system as described elsewhere⁵.

Exposure Experiments and Data Treatment

Various microenvironments were chosen for air sampling based on the anticipated presence of elevated levels of one or more VOCs. Through the evaluation of a range of microenvironments, insight into the types of environments that contribute to human exposure would be obtained. Based on the VOC levels found, a subset of these environments was selected for human exposure experiments to see if these microenvironments led to elevated levels of VOCs in exhaled breath. For each of the human exposure experiments a volunteer spent an average of four hours in the selected environment. After this time, the person was removed from the exposure situation and samples of exhaled breath were collected at multiple times over the next 3.5 h. When collecting alveolar breath samples using the new spirometer mentioned above⁷, these time points were 3, 8, 18, 28, 38, 53, 68, 98, 128, 173, and 218 minutes after exposure. Whole breath samples were also collected in some experiments for either a comparison to those collected using the alveolar device or for those chemicals more appropriately sampled using Tenax-GC. In addition to collection of a breath sample just before the start of the exposure, canister air samples were collected the night before the exposure, during the exposure, and during sample collection, to help identify potentially confounding exposures.

The VOC concentrations in these breath samples were studied as a function of time, and fit to equations of the form $A = C e^{-E t}$ and $A = C_1 e^{-E_1 t} + C_2 e^{-E_2 t}$ corresponding to a one and two compartment pharmacokinetic decay, respectively, where A is the concentration in the breath at any time t; C, C₁, and C₂ are constants; and E, E₁ and E₂ are the exponential constants that reflect the rate of decay. This curve fitting was accomplished using NLIN, a nonlinear curve fitting routine incorporated into SAS software (SAS Institute, Cary, NC). By defining the half-life (t_{1/2}) to be the time needed for the breath concentration to be reduced by one half, the calculated exponential constant was used to solve for t_{1/2}. The half-lives for the two compartment model were found in the same manner using E₁ and E₂ independently.

Results

Microenvironmental Screening

Air samples from a total of 32 microenvironments were analyzed in this study. The environments included a copy center, areas with wood staining activities, areas with oil-based painting activities, wood and metal shops,

a furniture stripping shop, two hardware stores, two interior decorating stores, two beauty schools, homes using consumer products such as moth crystals, a home garage, an auto and mower refueling area, a paint and body shop, an indoor swimming pool, a bar/club with smokers, and diapers soaking in bleach. The concentrations of the target compounds found in some of these environments are shown in Table I. It can be seen that a wide range of aliphatic, aromatic and chlorinated chemical vapors was detected. This demonstrates that areas with the potential for exposure to a variety of VOCs are ubiquitous.

Exposure Experiments

Exposure experiments were conducted in the furniture stripping shop, indoor swimming pool, hardware store, a home garage with refueling and wood staining operations, and in an environment where consumer products were in use. This last exposure was staged because of the desire for information on p-dichlorobenzene, α -pinene, and limonene. The first of these three chemicals is found in moth crystals, and the last two can be found in lemon scented wood polish, products commonly used in the home. In general, exposure air concentrations of greater than $100 \mu\text{g}/\text{m}^3$ resulted in measureable levels of the compound in breath. Even at this low exposure level, it was often possible to measure a decay of the compound as it was eliminated from the body through breath. The short time required for the alveolar sampling device to collect the sample resulted in a greater number of data points than did the whole breath spirometer. The rapid collection of samples during the initial phase of the decay is necessary to characterize the elimination of the VOC from the blood, or first compartment in the compartmental description of the body.

The body is often thought of as consisting of a series of compartments. As a chemical is inhaled, it can partition into the blood through the lung. From here it can be carried to other tissues or groups of tissues, e.g., vessel-rich group or fat tissue, and stored at rates dependent upon the relative solubility of the VOC in the tissue (blood:tissue partition coefficient) and the rate at which that tissue is perfused. Upon termination of the exposure, the remaining parent VOC is released (some can be lost to metabolism) via the reverse process. Through a classical pharmacokinetic analysis of the data, the relative compartmental distributions can be determined from the C values (not presented here) in addition to the information about residence times already mentioned. This type of analysis begins to address the issue of dose, that is, concentration times time, to a compartment; this is the most relevant toxicological information. If the appropriate partition factors and perfusion rates are known, physiologically based pharmacokinetic (PBPK) modeling can be used to study the doses various target organs. Such models can become quite complex¹¹ and were beyond the scope of the current study.

Residence half lives calculated from the exponential coefficients for the VOCs in this study are shown in Table II. Both one- and two-compartment models were used. Data were not collected at sufficiently long times after exposure to permit mathematical analysis with a number of compartments greater than two. Values presented are derived from the alveolar decay data except for α -pinene, limonene, and p-dichlorobenzene, which were collected and analyzed using whole breath with Tenax-GC based collection and analysis. Based on an analysis of the data using the F-test, the two compartment model provided for a better mathematical representation

of the data¹⁰. The generally short first half lives represent the elimination of the VOC from the blood. Such rapid changes require frequent measurement; the alveolar spirometer allowed for increased sample collection capability relative to the whole breath spirometer.

Conclusions

The general results of the microenvironmental screening provide an interesting snapshot of potential VOC exposure possibilities, but one which should not be extended to all similar microenvironments or activities. The results of the exposure experiments show that information on VOC elimination through breath can be obtained for low-level exposures without the use of an exposure chamber. The fact that decays were measured indicates that low levels of VOCs can accumulate in the body. The toxicological significance of such doses remains to be determined.

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TABLE 1. AIR CONCENTRATIONS ($\mu\text{g}/\text{m}^3$) IN MICROENVIRONMENT SCREENING
CANISTER SAMPLES

Compound	Photocopy & Print Center	Oil-Based Painting	Metal Shop	Wood Staining	Home No. 2 With Moth Crystals	Indoor Swimming Pool	Furniture Stripping Shop
Vinyl chloride	ND ^a	ND	ND	ND	ND	ND	ND
Isopentane	ND	ND	ND	ND	3	24	10
n-Pentane	180	150	62	1100	3	15	6
Vinylidene chloride	ND	ND	4	ND	ND	ND	3
2-Methylpentane	2	ND	12	58	3	7	26
Dichloromethane	10	25	23	2	77	ND	7100
Chloroform	50	77	36	ND	ND	240	2
1,1,1-Trichloroethane	5	3	21000	18	34	2	280
Carbon tetrachloride	ND	ND	ND	ND	ND	ND	ND
Benzene	6	ND	ND	10	2	6	4
Trichloroethylene	ND	5	8	5	ND	ND	120
Toluene	9	20	130	2700	61	7	2500
n-Octane	ND	16	27	350	1	1	29
Tetrachloroethylene	ND	ND	1200	2	ND	ND	23
Ethylbenzene	1	24	4	11	47	3	120
m,p-Xylene	5	88	11	30	180	10	430
n-Nonane	2	230	26	340	5	2	61
p-Xylene	4	39	4	11	11	4	160
Styrene	ND	ND	ND	2	ND	ND	68
n-Decane	ND	1200	63	810	9	4	180
p-Dichlorobenzene	ND	ND	ND	ND	>540	18	ND
n-Dodecane	ND	46	NC ^b	NC	3	ND	35

(continued)

TABLE 1. AIR CONCENTRATIONS ($\mu\text{g}/\text{m}^3$) IN MICROENVIRONMENT SCREENING
CANISTER SAMPLES (continued)

	Hardware Store No. 1	Interior Decorating Store No. 1	Beauty School No. 2	Bar/Club with Smokers	Auto & Mower Refueling	Paint & Body Shop	Home Diapers In Bleach
Vinyl chloride	ND	ND	ND	ND	1	ND	ND
Isopentane	29	35	43	74	>1500	260	20
n-Pentane	16	19	11	27	>3600	110	16
Vinylidene chloride	2	ND	ND	ND	1	ND	ND
2-Methylpentane	41	12	3	22	>1900	61	ND
Dichloromethane	900	240	ND	6	NC	7	41
Chloroform	ND	ND	6	6	NC	1	94
1,1,1-Trichloroethane	210	22	8	3	2	3	ND
Carbon tetrachloride	ND	ND	ND	ND	NC	ND	ND
Benzene	9	9	8	20	>380	68	4
Trichloroethylene	ND	ND	7	ND	ND	ND	ND
Toluene	650	310	320	54	920	2100	11
n-Octane	80	21	ND	2	22	35	ND
Tetrachloroethylene	27	9	4	1	ND	ND	ND
Ethylbenzene	590	28	2	10	110	67	1
m,p-Xylene	1700	93	8	31	340	220	7
n-Nonane	290	380	3	6	20	36	2
p-Xylene	110	22	2	13	120	80	2
Styrene	38	6	ND	6	13	19	2
n-Decane	570	700	2	7	10	5	3
p-Dichlorobenzene	39	ND	3	NC	NC	NC	NC
n-Dodecane	57	NC	2	NC	NC	NC	NC

^aND = not detected.

^bNC = not calculated.

TABLE II. CALCULATED HALF-LIVES FOR VOCs IN THIS STUDY

Compound	Exposure Air Level ($\mu\text{g}/\text{m}^3$)	Participant	One Compartment	Two Compartment	
			$t_{1/2}(\text{h})$	First $t_{1/2}(\text{h})$	Second $t_{1/2}(\text{h})$
Aliphatic Hydrocarbons					
n-Pentane	3400	1	0.70	0.08	2.34
	340	1	1.15	0.07	2.07
	320	1	0.67	0.19	2.84
n-Octane	12000	1	1.37	0.02	1.73
	210	2	1.13	0.06	2.01
	210	1	0.68	0.15	2.06
	180	2	0.08	0.02	0.48
n-Decane	130	3	0.21	0.04	1.53
	14000	1	1.35	0.18	2.33
	360	2	0.22	0.08	1.39
	360	1	0.17	0.04	1.06
n-Undecane	210	3	0.27	0.19	2.82
	5600	1	0.28	0.07	1.36
	1000	1	0.65	0.08	2.33
2-Methylpentane	2000	1	0.86	0.21	3.18
2-Methylhexane	340	1	0.26	0.13	3.16
3-Methylhexane	410	1	0.39	0.13	2.54
2-Methyloctane	5400	1	0.60	0.28	2.48
Ethylcyclohexane	900	1	0.89	0.19	2.53
α -Pinene	97	2	0.79	0.13	1.60
Limonene	160	2	2.43	0.24	6.88
Aromatic Hydrocarbons					
Benzene	430	1	1.68	0.14	3.38
Toluene	5700	1	0.82	0.10	1.82
	1200	1	1.84	0.05	2.64
	640	2	1.53	0.07	1.88
	640	1	1.06	0.08	1.68
	460	3	1.13	0.05	4.05
	320	2	0.52	0.27	3.23
Ethylbenzene	2600	1	2.46	0.03	2.90
	360	2	0.22	0.08	2.12
	150	2	1.70	0.04	2.49
	150	1	1.02	0.08	1.43
m,p-Xylene	1600	2	0.92	0.03	1.10
	560	2	0.64	0.13	2.42
	560	1	0.45	0.11	2.15
	230	3	0.08	0.03	2.16
	160	4	0.58	0.08	2.12
o-Xylene	700	1	0.67	0.11	2.94
	440	2	0.25	0.08	1.17
	190	2	1.61	0.04	9.95
Halogenated Hydrocarbons					
Dichloromethane	5000	1	0.60	0.13	1.80
	470	2	0.40	0.10	1.07
	320	3	1.65	0.08	1.14
	220	4	1.86	0.17	2.07
Chloroform	600	2	0.72	0.08	1.58
1,1,1-Trichloroethane	16000	1	0.88	0.10	1.90
	340	2	1.33	0.13	2.60
	200	1	0.99	0.17	3.18
	200	4	3.39	0.17	6.08
	140	1	1.00	0.08	1.80
Tetrachloroethylene	280	2	2.42	0.18	3.70
	190	3	0.85	0.11	1.67
p-Dichlorobenzene	9400	2	1.57	0.53	21

AUTOMATED SPECIFIC ANALYSIS OF BREATH WITH A PORTABLE MONITOR

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Breath analysis can be an important and often useful measurement in assessing exposure to certain pollutants. Alcohol and carbon monoxide are two examples of compounds that are accumulated in the body and excreted slowly when exposure ceases. In the quest for a better breath alcohol monitor, we have studied the development of techniques for self-calibration that can be incorporated into analytical instruments of all kinds. One of these promising techniques is dynamic coulometry.

Amperometric electrochemical sensors operate in a destructive mode: the sample is oxidized or reduced, producing a current at the working electrode which is the output signal. Dynamic coulometry is carried out with two sensors connected in series. If the flow through them is made reversible, they can be made to calibrate one another. In this paper, we investigate some of the assumptions of dynamic coulometry. It appears that it may be possible to construct an instrument that need only be calibrated when sensors are installed, even though not all the assumptions of the technique are supported.

Introduction

We have been pursuing the development of dynamic coulometry, a modification of amperometric gas detection, that promises to reduce the need for frequent calibration of analytical instruments. The work discussed in this paper concerns portable alcohol analyzers, but the method may find application to any electrochemically-active analyte.

Blood alcohol monitors are needed by agencies involved in the detoxification and treatment of alcohol abusers. In the former case, the care provider needs objective assurance that the patient is adhering to an abstinence regime; many patients resort to elaborate strategies to obtain alcohol and to disguise their use of it.

Although blood alcohol levels are the most accurate indicator of exposure, in the case of alcohol and carbon monoxide, the blood levels are directly related to the concentrations of these compounds in alveolar air (1). Monitoring the breath is faster, easier, cheaper, and much less invasive than a blood test.

Breath alcohol instruments, or "breathalyzers", have been marketed for many years, but there are many areas for improvement (2,3,4,5). An instrument that is resistant to interferences and can perform automatic calibration (or does not need calibration) is very much needed in many applications. Recent newspaper reports, for example, have described the dismissal of DUI cases because police officers were calibrating their breathalyzers at home. Employers, such as managers of truck and taxicab fleets, also require instruments of this kind, whose very presence in the workplace will reduce the incidence of alcohol abuse on the job. A device that is useful for this purpose must be very selective in order to distinguish between alcohol and common interferents such as acetaldehyde and carbon monoxide, as well as to foil deliberate attempts to trick the meter. Since the user population is medically- rather than technically-oriented, the device should not involve the user unnecessarily in the details of its operation.

Dynamic coulometry makes use of the fact that amperometric gas sensors consume a fraction of the analyte that enters them (6,7). This fraction is the "efficiency", since the oxidation of the analyte produces an electric current that constitutes the signal output of the sensor. The higher the efficiency, the greater the current, and the more analyte is consumed. If two such sensors are connected in tandem and configured for reversible flow, each can measure the efficiency of the other. When the output current of the sensor is divided by its efficiency, an estimate of the current generated by oxidation of 100% of the analyte is obtained (Equations 1-3). This can be converted directly to an absolute measurement of concentration.

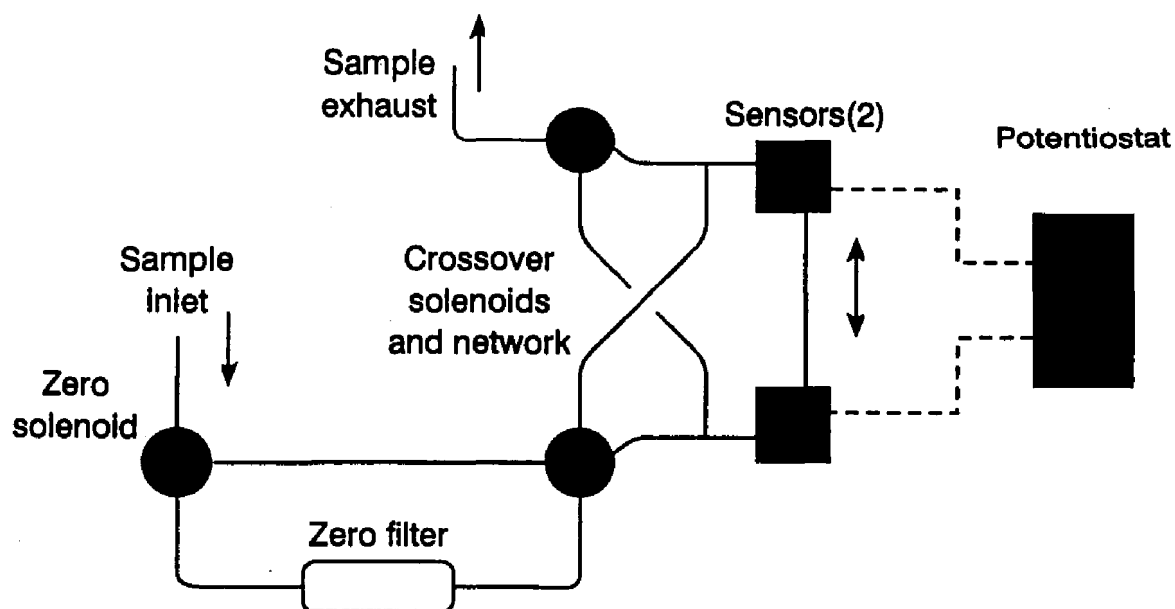
An important feature of this project has been that the proposed instrument will be able to perform a true "calibration" automatically and without the need of on-board standards or user intervention. In addition, it will be sufficiently selective to eliminate most common accidental or deliberate interferences. Dynamic coulometry developed for alcohol monitoring might be applied to other measurements such as NO_2 , NO , formaldehyde, and H_2S . It may significantly reduce the time and money spent in daily, weekly or monthly calibration of health and safety instrumentation.

Experimental Methods

An experimental test bed was set up according to Figure 1. The twin solenoids caused the reversal of flow when actuated. To find low-power solenoids with low airflow resistance was not a trivial task; the solenoids used were pre-production prototypes supplied by The Lee Company. The sensors were standard carbon monoxide sensors manufactured by Transducer Research, Inc. They were selected by choosing pairs of sensors with similar outputs. The sample flowrate, which is critical in these experiments, was controlled by a small graphite-vane pump and needle valve, and the flowrate was measured with an electronic bubble flowmeter (The Buck Mini-Calibrator, A.P. Buck, Inc., Orlando, FL). The operation of the apparatus and the logging of data were controlled by a battery-operated microcontroller (Onset Computer Corp., North Falmouth, MA) and suitable custom-made interface circuits. Datafiles produced by the apparatus were processed using Lotus spreadsheets.

Dilutions of alcohol, acetone, acetaldehyde, and acetoacetone were made by injecting a measured amount of the liquid into a Tedlar gas sample bag and filling the bag with air. Dilutions of carbon monoxide were made by mixing a certified mixture from a cylinder with air using a pump, flowmeter, and stopwatch.

Figure 1. Schematic of the apparatus used for these experiments. Solenoids and potentiostat were controlled by a miniature datalogging computer.



Results

Dynamic Coulometry

The potential of dynamic coulometry has been previously demonstrated for carbon monoxide (7). Operation was therefore tested by passing 40 ppm CO into the apparatus at a flowrate of 10.4 mL/min. The zero-corrected results are shown in Figure 2. With the gas movement in the forward direction, the output of sensor A is greater than that of sensor B; when it is reversed, the output of A decreases, and that of B increases. This is the pattern expected in a dynamic coulometry experiment. A substantial proportion of the CO is removed from the sample by each sensor. In this particular experiment, the response of sensor B was judged to be very slow, and the outputs of both sensors were very weak. This judgment was based on the following calculation:

Carbon monoxide at 40 ppm contains $1.786 \cdot 10^{-6}$ mole/liter. At a flowrate of 10.4 mL/min, this is equivalent to $2.92 \cdot 10^{-10}$ mole/sec. For the two-electron oxidation to carbon dioxide, the current generated by 100% oxidation of ethanol supplied at this flow rate can be calculated to be 56 microamperes. The maximum currents measured in this analysis are 8.86 and 8.70 microamps for sensors A and B, respectively. The corresponding decreases in the signal due to depletion of the sample by the upstream sensor are 26.2% and 27.0%. The calculated currents for 100% oxidation are therefore $8.86/.270 = 32.8$ microamps and $8.70/.262 = 33.2$ microamps. These values are low compared to the expected 56 microamps and may be due to several causes, from a mistake in diluting the gases, to an invalid assumption in the technique itself.

Both sensors were replaced by new ones for the remainder of these measurements, and satisfactory results were obtained. Ethanol vapor was run at a flowrate of 11.9 mL/min and concentrations of 12, 51 and 96 ppm. The plot of sensor output versus concentration is shown in Figure 3. The calculations of dynamic coulometry are shown in Table I. The two complex terms R_a and R_b are equivalent to the current expected from 100% reaction of the analyte, and are derived from the theoretical treatment of dynamic coulometry (Stetter and Zaromb, 1983):

$$X_A = C.R_a/V, \text{ where } R_a = I_A f \cdot I_B r / (I_B r - I_B f) \quad (\text{Eq. 1})$$

$$X_B = C.R_b/V, \text{ where } R_b = I_A f \cdot I_B r / (I_A f - I_A r) \quad (\text{Eq. 2})$$

$$C = RT/zFp \quad (\text{Eq. 3})$$

where X_i = mole fraction of the vapor

V = the volumetric flowrate

I_i = observed currents in sensors A or B in the (f)orward or (r)everse directions of gas flow

C is a composite of the gas constant R , Kelvin temperature T , number of electrons in the reaction z , Faraday constant F , and atmospheric pressure p

Figure 2. A test of the dynamic coulometry apparatus using CO. The scales of sensors A and B have been changed so the lines do not overlap.

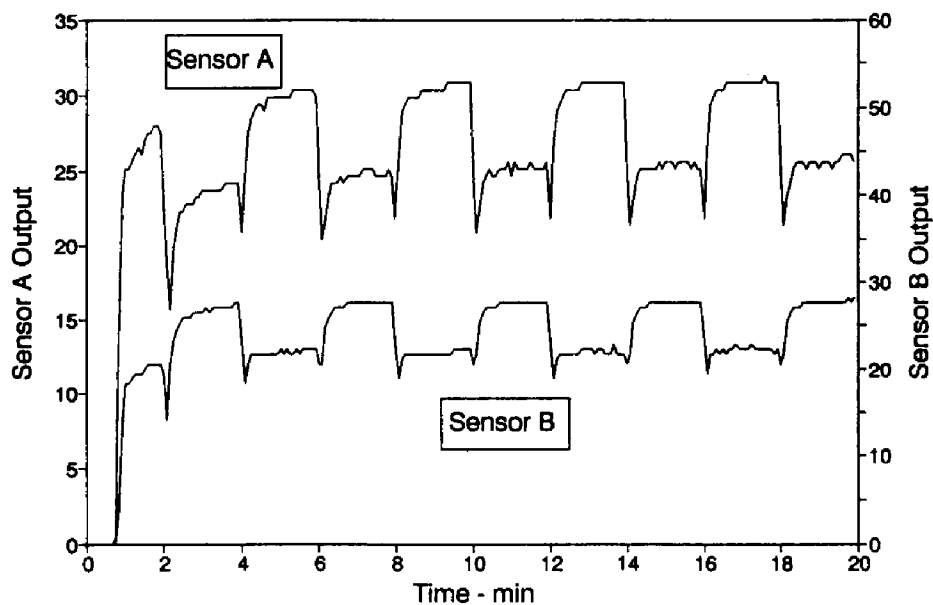


Figure 3. The maximum current outputs of the sensors are linear with concentration.

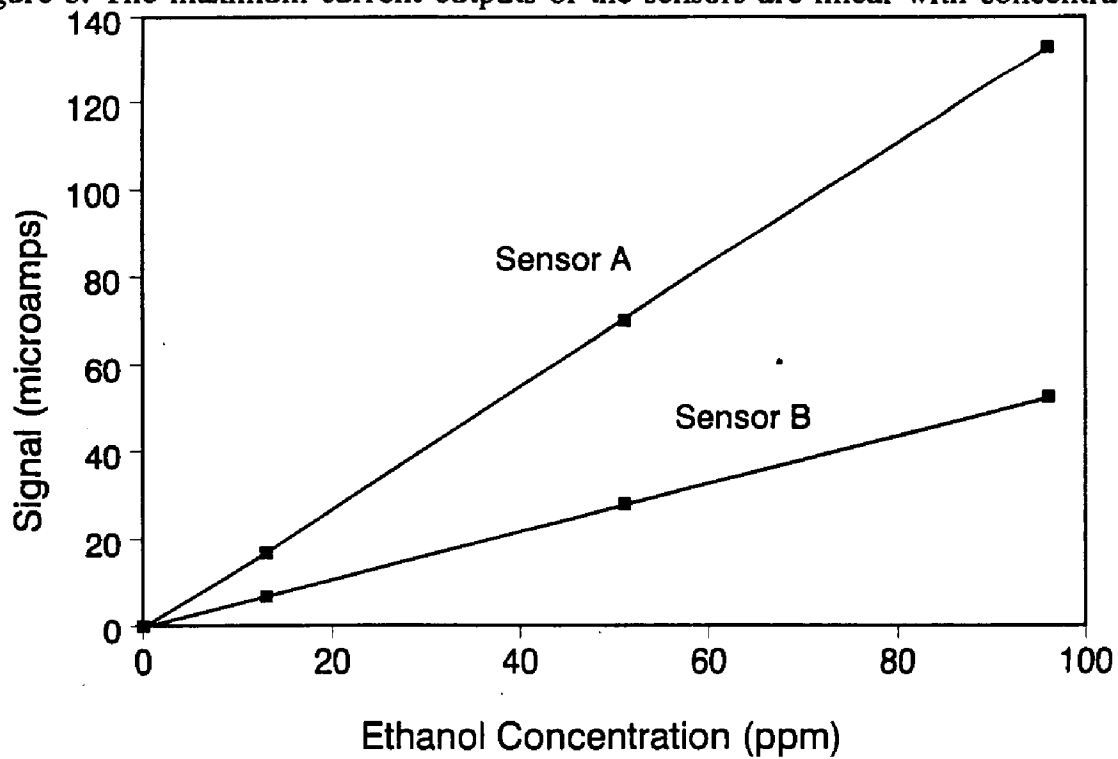


Table I. DCO calculations for ethanol vapor. 50 ppm of ethanol in air was pumped through the instrument at a flowrate of 11.9 mL/min. The terms Ra and Rb are explained in the text and correspond to the expected current output of the sensors if the ethanol were 100% consumed.

Concentration (ppm)	Net Signal	Sensor A Effic- iency	Ra	Net Signal	Sensor B Effic- iency	Rb
(ppm)	(uA)	(%)	(uA)	(uA)	(%)	(uA)
12.5	16.7	.179	93.3	6.75	.182	37.1
53	69.9	.174	380	27.9	.186	160
95	133	.170	739	52.4	.180	308

The terms Ra and Rb should be identical for both sensors in a given experiment, and they should be proportional to analyte concentration and inversely proportional to flowrate. In this experiment, the values of Ra and Rb were plotted against concentration in Figure 4 and compared to the expected current for 100% oxidation.

It is immediately clear that, although one sensor closely follows the theoretical prediction for 100% oxidation, the remaining sensor yields a calculated value that is about 60% too high. In order to confirm the reality of this unexpected result, the experiment was repeated using carbon monoxide, which has previously been shown to be a good analyte for DCO (7). These results are shown in Figure 5, and lead to the same conclusion as the experiment with ethanol.

At this time, we do not understand the reasons behind this discrepancy. Obvious sources of error were checked: instrument calibration, flowrate, leaks, etc. We next examined both the explicit and implicit assumptions made in deriving the DCO theory. Violations of most of these assumptions would result in a negative error in the calculated 100% oxidation current. One implicit assumption remained as a possible cause of the discrepancy: We have assumed that the efficiency of a sensor would be the same in both the forward- and reverse-flow directions. If not, either positive or negative errors could result. Testing of this assumption will require further investigation.

In spite of the departure from theoretical prediction, it should be pointed out that the Ra and Rb were nevertheless linear with flow rate. This observation is sufficient to demonstrate the validity of DCO in this application. An empirically-derived, or coulometric, constant can be derived by calibration rather than by calculation from Equation 3. Presumably, an instrument using DCO should only need to be calibrated when a new sensor is installed.

Figure 4. The total oxidation current for ethanol is linear with flowrate in spite of the change in sensor efficiency.

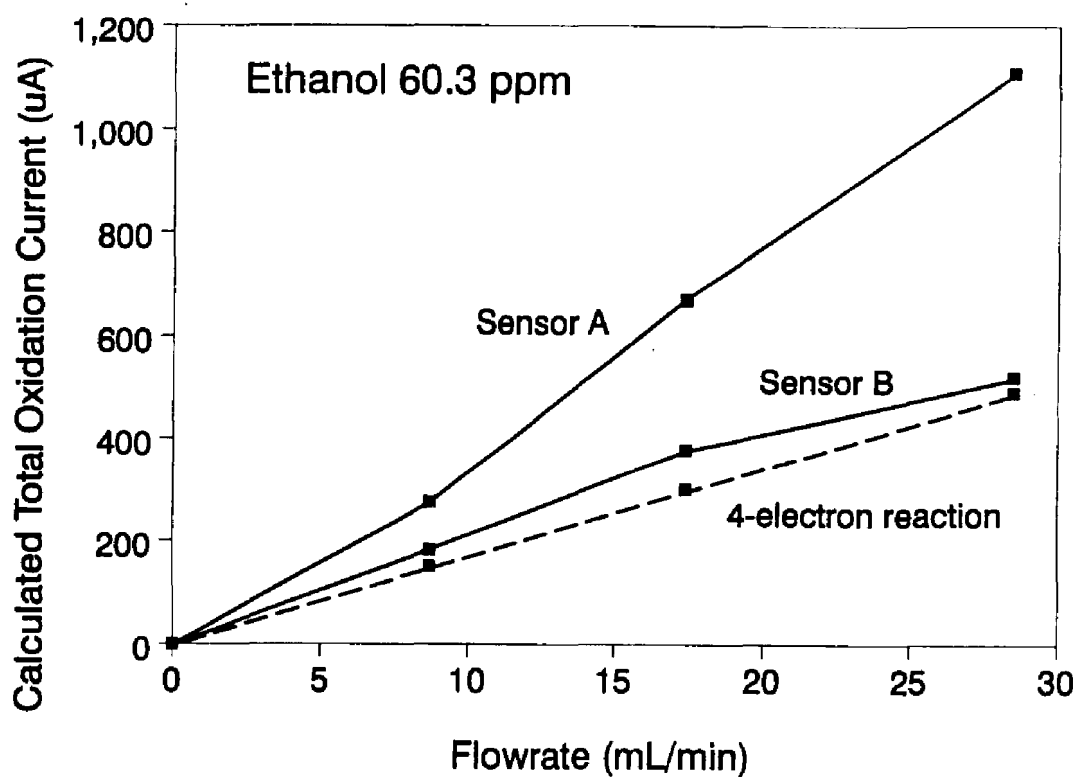
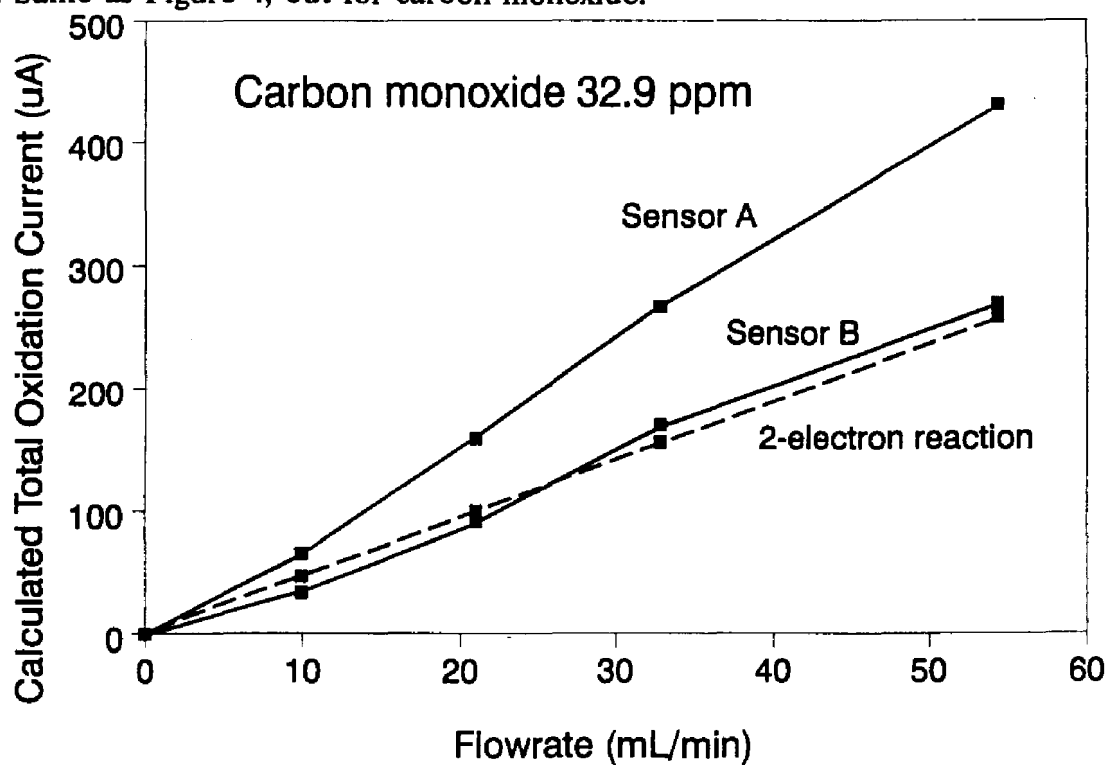


Figure 5. Same as Figure 4, but for carbon monoxide.



The success of the dynamic coulometry experiments led us to attempt a few brief experiments with static coulometry, in which a measured volume of sample vapor is trapped in the chamber of a single sensor. As the analyte is consumed by the sensor, the signal should decrease in a logarithmic fashion (if the gas is well-mixed in the chamber). This experiment was done by arranging the two solenoids on either side of a single sensor, to direct the sample stream either through the sensor or around it. When the stream was diverted, the fall of the signal was observed for a fixed time. The area under the curve (in microampere-seconds, or microcoulombs) should represent the total ethanol in the volume of sample.

Both the fall of the signal and its logarithmic nature were observed in these preliminary experiments (Figure 6). An instrument employing static coulometry would be simpler and perhaps just as effective as one using dynamic coulometry.

Responses of Different Sensors and Interferents

Potential interferences in measuring alcohol on the breath are acetaldehyde, acetone, acetoacetone, and carbon monoxide. The last of these can be found in the breath of smokers. The others are metabolites of alcohol, but can be found in the breath of some individuals with metabolic diseases. Carbon monoxide has already been run; the other three compounds were tested using the same program. The results are shown in Table II. The responses of acetaldehyde and acetone are very weak, only 2.5-4% of that of ethanol. Acetoacetone gives a strong but sluggish response, rising slowly over the course of the experiment (Figure 7). Since the signal strength due to acetoacetone was similar to that of ethanol, this would be a serious interference. Ethanol (50 ppm) and acetoacetone (27 ppm) were mixed in the same bag and run together (Figure 8). The ethanol signal is clearly distinguishable over the acetoacetone signal, and could be separated in a computer by suitable digital filtering of the signal.

Responses of the platinum sensor to ethanol and some interferents were measured at several bias potentials. The results are shown in Table IV. The ethanol response does not change over the bias range of -50 to 200 mV, and the change in the carbon monoxide signal is less than twofold. Selectivity to these analytes therefore cannot be improved by manipulating the bias potential.

A sensor with a high-surface-area gold working electrode was installed temporarily in the apparatus and exposed to 221 ppm hydrogen sulfide (a positive control), 334 ppm carbon monoxide, and 278 ppm ethanol. Neither carbon monoxide nor ethanol produced any response on the gold electrode.

Figure 6. Acetoacetone elicits a sluggish response from the sensor.

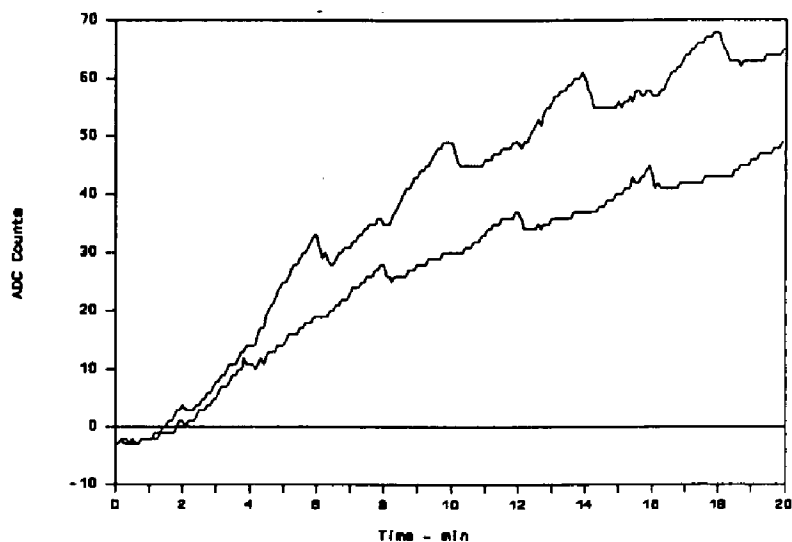


Figure 7. The signal for ethanol is clearly distinguishable from that of acetoacetone.

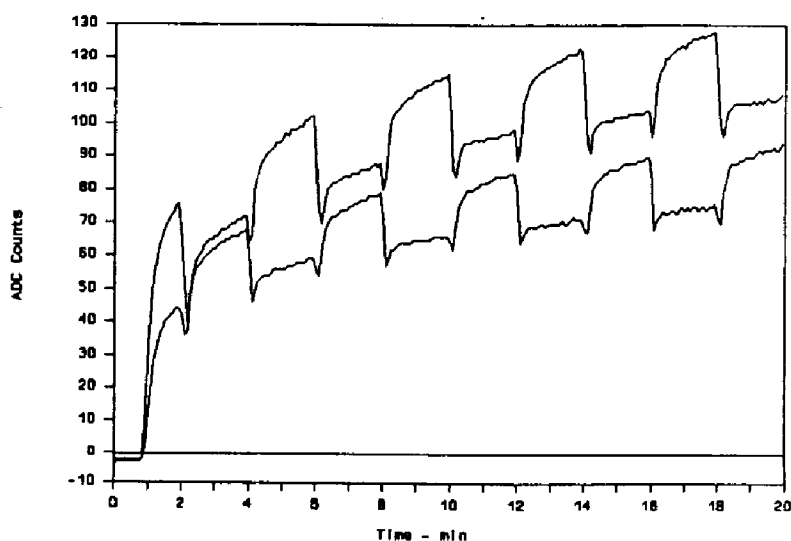


Figure 8. Static coulometry of ethanol. The descending line, when appropriately plotted, fits a semilogarithmic relationship with time.

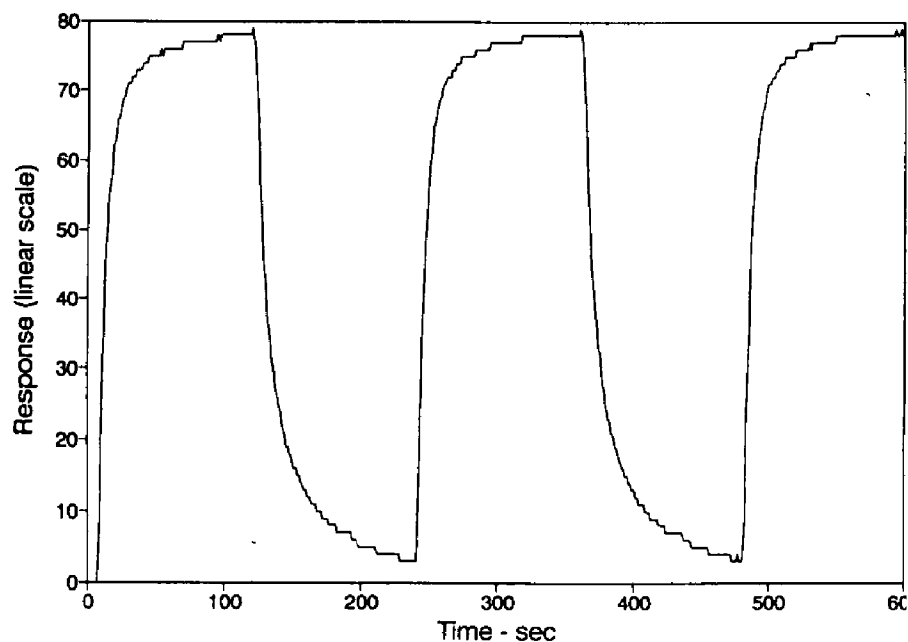


Table II. Responses of platinum- and gold-electrode sensors to ethanol and its metabolites.

Analyte, concentration and bias used	Outputs in microamps/ppm	
	Sensor A	Sensor B
ethanol, +100 mV 60.3 ppm	1.52	0.86
carbon monoxide, +100 mV, 33 ppm	0.77	0.50
acetone, - 100 mV 43 ppm	0.028	0.025
acetone, + 100 mV 43 ppm	no signal	no signal
acetoacetone, -100 mV 27 ppm	(0.63) slowly and continuously rising signal	(0.48) slowly and continuously rising signal
acetoacetone, +100 mV 27 ppm	(1.05) slowly and continuously rising signal	(1.08) slowly and continuously rising signal
acetaldehyde, +100 mV 48 ppm	0.038	0.023

Conclusions

Coulometry (either dynamic or static) is a potentially useful method for measuring alcohol and carbon monoxide. The method may ultimately be used for other gases as well. These methods offer the promise of instruments that will require only infrequent calibration. Although the sensors did not produce the current predicted by the theoretical development of the dynamic coulometry technique, the following relationships, derived from the the theoretical development, were shown to hold:

- * Peak sensor output was linear with concentration.

- * The calculated 100% oxidation current extrapolated from the measured signal was independent of the efficiency of the sensor.

In this work, we also demonstrated that the common metabolites of alcohol, acetaldehyde, acetone, and acetoacetic acid, produced signals that were either weak or easily distinguished from that of alcohol. Carbon monoxide, however, is a serious interference, and will have to be dealt with by special means.

Acknowledgments

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ROUTES OF CHLOROFORM EXPOSURE FROM SHOWERING WITH CHLORINATED WATER

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Abstract

Showering is the single, largest use of water in the home. This activity results in exposure to volatile organic compounds (VOC) present in the water that are released to the air and contact the skin. Inhalation and dermal exposure increases the body burden when the compounds penetrate the body barrier. The concentration of VOC in exhaled breath is related to the body burden and was used to estimate the relative internal chloroform dose from inhalation and dermal exposures during showering with chlorinated water. Thirteen normal showers, which include inhalation and dermal exposure, and thirteen inhalation only studies were analyzed using typical showering conditions. The post-exposure breath chloroform concentrations ranged from 6.0 to 21 $\mu\text{g}/\text{m}^3$ for normal showers and 2.4 to 10 $\mu\text{g}/\text{m}^3$ for inhalation only exposure, while the pre-exposure concentrations were less than the minimum detection limit of 0.86 $\mu\text{g}/\text{m}^3$. The elevated chloroform concentration in breath after exposure depended upon the water concentration, water temperature, exposure duration, and the post-exposure delay time prior to collecting the breath sample. To facilitate comparison of the body burden all parameters, other than water concentration, were fixed for the study. A statistically significant difference was found between the breath concentration after showering (dermal plus inhalation exposure) and after breathing air in a shower stall (inhalation only exposure). It was determined that the inhalation and dermal exposures contributed approximately equally to the elevated chloroform body burden resulting from showering.

Introduction

Showers have been proposed to be a major indoor air source of VOC (1,2) since it uses large amounts of heated water which results in the release of the VOC contained in the water. Chlorinated water contains $\mu\text{G}/\text{L}$ quantities of chloroform, which is formed as a by-product of the chlorination process (3). The showering individual is highly exposed to the chloroform released since not only is he or she breathing the elevated air concentrations within the stall but the entire body is contacts water containing chloroform. Recently, several studies (1,2,4-6) have indicated that exposure to VOC from showers or bathing may be as large as or larger than exposure from ingestion alone. These studies have estimated inhalation exposure to volatile organic compounds (VOC) in shower air using unoccupied shower laboratory chambers (1,2,4). Dermal exposures have been calculated from equilibrium considerations and skin permeability estimates (5,6). The present study measured exposure and body burden changes of individuals exposed to shower water or air within a shower stall (7). In addition, parameters that control the amount of exposure to chloroform were examined and the relative increase in body burden due to dermal and inhalation exposure from showering with chlorinated tap water quantified.

Methods

Sampling

Exhaled breath samples were collected from subjects by having them breathe through a non-rebreathing two-way valve attached to a Tedlar sampling bag. The subjects were supplied with purified, humidified air through the valve from an inhalation bag. Breath from the collection bag was transferred to a Tenax packed trap. Water samples were collected from the tap in the same room as the shower using clean 50 mL vials, following EPA Method 502.1 (8). Ten minute breathing zone air samples were collected in the shower stall at a flow rate between 750 and 1250 cc/min using Tenax traps.

Analysis

The breath and air samples were analyzed by thermally desorbing the trap and transferring the compounds to a packed column gas chromatograph with an electrolytic conductivity detector in the halogen-specific system mode. The water was analyzed by purge and trap-gas chromatography following EPA method 502 (8).

Quality Assurance

A blank and external standard was analyzed daily to monitor the response of the GC. Typically, the blank concentrations were below the detection limit, thus any response indicated contamination in the system. The response of an external standard was compared to the value calculated from a calibration equation. If the response differed by more than $\pm 20\%$, a new calibration equation was determined. The precision of the desorption and water analytical systems for chloroform were 13% and 10%, respectively. The minimum detection limit (MDL) of the desorption and water analytical system were 13 nG and 0.65 $\mu\text{G/L}$, respectively.

Experiment I - Evaluation of Parameters

A model shower, constructed of stainless steel, was used to evaluate the effect of water temperature and duration of inhalation exposure on the breath concentration. Water was sprayed within the chamber using a standard shower head at two temperatures, 34°C and 41°C, and the subject breathed the air from chamber for 5, 10 or 15 minutes. A standard, full size shower was used to evaluate the relationship between the chloroform air concentration within the shower stall and the water concentration, with and without a subject present. For this and all full size shower studies a shower duration of 10 minutes and a water temperature of 40°C was used. All other controllable parameters were fixed for all experiments including: the water flowrate (8.7 L/min), shower head setting, ventilation system being off and post exposure delay prior to collection of a breath sample (5 minutes). The chloroform water concentration was measured whenever an air or breath sample was collected.

Experiment II - Chloroform Exposure from Inhalation Only

Six subjects (4 males and 2 females) participated in thirteen inhalation only exposure experiments using the same full-size shower, shower parameters and protocols as in Experiment I. Each subject stood next to the water stream within the shower stall for ten minutes, thereby exposing the individual to chloroform vaporized from the water. The subject wore rubber clothes and boots during the experiment to avoid dermal contact with the shower water. Breath samples were collected from the subject prior to each inhalation only exposure and five minutes after exposure. Air and water samples were collected during each exposure.

Experiment III - Chloroform Exposure from Normal Showers

Thirteen showers were taken by six subjects (5 males and 1 female) to estimate total chloroform exposure from a typical shower. Breath samples were collected from each subject prior to and five minutes after each shower. Air and water samples were collected with each shower. All showering conditions were set as indicated in Experiment I. The data obtained from Experiment II and Experiment III were used to compare the chloroform body burden resulting from a normal shower with that from an inhalation only exposure. The comparison was conducted using a covariance analysis.

Results and Discussion

The air chloroform concentration was measured with and without a showering individual present to determine whether the movement and splashing by an individual altered the air concentration and could therefore affect the inhalation exposure. As shown in figure 1 the air concentration/water concentration relationship for the two conditions overlapped. The mean and standard deviation of chloroform air concentrations without a showering individual were $157 \mu\text{g}/\text{m}^3$ and $75.5 \mu\text{g}/\text{m}^3$, respectively. The mean and standard deviation of air chloroform concentrations while an individual was showering were $186 \mu\text{g}/\text{m}^3$ and $76.0 \mu\text{g}/\text{m}^3$, respectively. The concentrations were compared using an F-test. The F-value was 0.01 at a $p=0.9294$, indicating the presence of an individual did not affect the chloroform air concentration. μg

The breath concentrations measured after exposure to air in the model system demonstrated that both exposure duration and water temperature altered the body burden (Table 1). The breath concentration was found to be positively correlated with water temperature and exposure duration. Each temperature and duration was found to be statistically significant by both ANOVA and Duncan's Test.

The shower air concentration were observed to increase with water concentration. The shower air concentration ranged between 69 and $330 \mu\text{g}/\text{m}^3$ for a water concentration range of 12.9 and $40.0 \mu\text{g}/\text{L}$ (figure 1). Chloroform was not detected in any of the air samples collected prior to the water being turned on. The relationship between the air and water concentration is described by the linear model:

$$C_{\text{air}} = 8.11 * C_{\text{water}} - 39.2 \quad \text{for } C_{\text{water}} > 4.8 \mu\text{g}/\text{L}$$

$$\text{with an } R^2 = 0.87 \text{ at a } P = 0.001$$

In addition to the air concentration increasing with water concentration, the body burden, as measured by breath analysis, increased, for both inhalation only exposure and for normal showers. Breath samples were collected prior to and after each exposure type. In all cases, chloroform was not detected in breath samples collected before exposure. Thus, the pre-exposure breath chloroform concentration was always less than the detection limit of $0.86 \mu\text{g}/\text{m}^3$. The breath concentrations after a normal shower, which includes both inhalation and dermal exposure, tended to increase with the chloroform concentration for water in the range 5.3 to $36 \mu\text{g}/\text{L}$ (figure 2). The mean and standard deviation of the breath concentrations were $13 \mu\text{g}/\text{m}^3$ and $3.9 \mu\text{g}/\text{m}^3$, respectively. Minimum and maximum breath concentrations were 6.0 and $21 \mu\text{g}/\text{m}^3$, respectively. Similarly, the breath concentrations after inhalation only exposures tended to increase with increasing water concentration for the range 10 to $37 \mu\text{g}/\text{L}$ (figure 2). The mean and standard deviation of breath concentrations measured after

inhalation only exposure were $7.1 \mu\text{g}/\text{m}^3$ and $2.5 \mu\text{g}/\text{m}^3$, respectively. Minimum and maximum breath concentrations after inhalation only exposures were 2.4 and $10 \mu\text{g}/\text{m}^3$, respectively. These two sets of breath samples were found to be significantly different using the F-test at a probability of $p=0.0001$.

Two explanations for a difference in the breath concentrations after the normal shower and inhalation only experiments are: 1) splashing of water by the showering individual increases the volatilization of chloroform and therefore the inhalation exposure and 2) dermal absorption of chloroform directly from the water occurs. The first explanation was shown not to be valid since the presence of an individual did not increase the air concentration above that measured in an unoccupied shower stall. Dermal absorption by non-polar hydrocarbons from dilute aqueous solutions has been demonstrated for a number of compounds (9) and has been predicted to contribute to the internal dose during showering based on theoretical considerations using estimates of permeation of compounds through the skin barrier and transfer rates within the body (6) and is the likely explanation for the results observed in this study.

The relative contribution from inhalation and dermal exposures were quantified based on the least mean squares (LSM) of chloroform breath concentration for the two exposures, while controlling for variations in the water concentration. The LSM of the breath concentrations resulting from a normal shower, which is a composite of inhalation and dermal exposures, was $13 \mu\text{g}/\text{m}^3$, while the LSM of the breath concentrations after inhalation exposures only was $6.8 \mu\text{g}/\text{m}^3$. The difference, $6.2 \mu\text{g}/\text{m}^3$, is assumed to be due to dermal exposure. The ratio of chloroform body burden increase from dermal exposure to that from inhalation exposure is therefore 0.93. Hence, both inhalation and dermal absorption contributed equally to the internal chloroform dose.

Conclusions

An increase in the chloroform body burden resulting from inhalation exposure and dermal exposure during a normal shower was observed in the present study. The breath concentration after showering was approximately twice as high as that after inhalation only exposure, indicating that the contribution to the internal dose by dermal absorption was equivalent to inhalation adsorption. The magnitude of the chloroform body burden increase was positively correlated with water concentration, water temperature and shower duration.

Acknowledgements

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Table 1

Breath concentration normalized to tap water concentration obtained after inhalation exposure for two water temperatures and three inhalation durations

Replicate Number	Warm (33.6°C)			Hot (40.8°C)		
	5 min	10 min	15 min	5 min	10 min	15 min
1	0.16	0.22	0.37	0.21	0.36	0.41
2	0.16	0.29	0.42	0.25	0.37	0.52
3	0.20	0.30	0.48	0.26	0.39	0.53
4	0.21	0.34	0.48	0.29	0.41	0.63
5	0.24	0.37	0.59	0.30	0.44	0.65

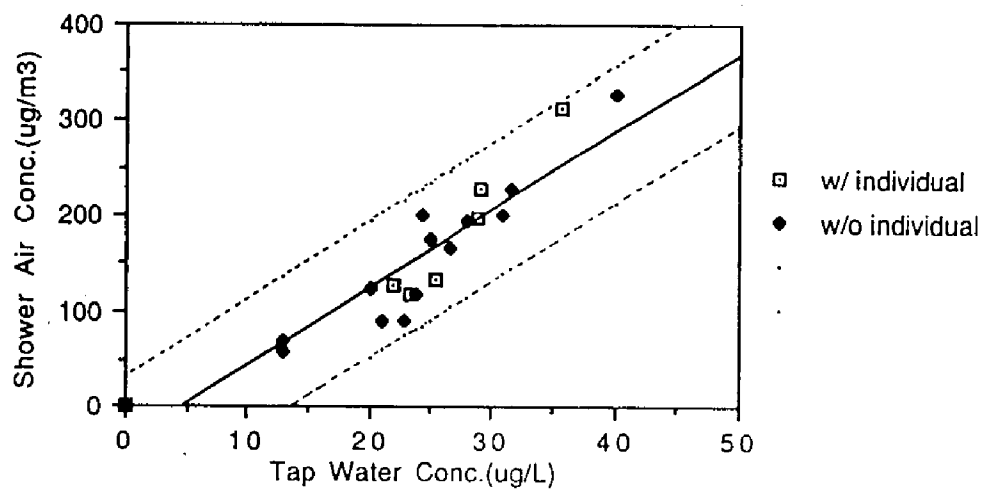


Figure 1. Chloroform shower air concentration with and without a showering individual versus tap water concentration (including 95% confidence interval).

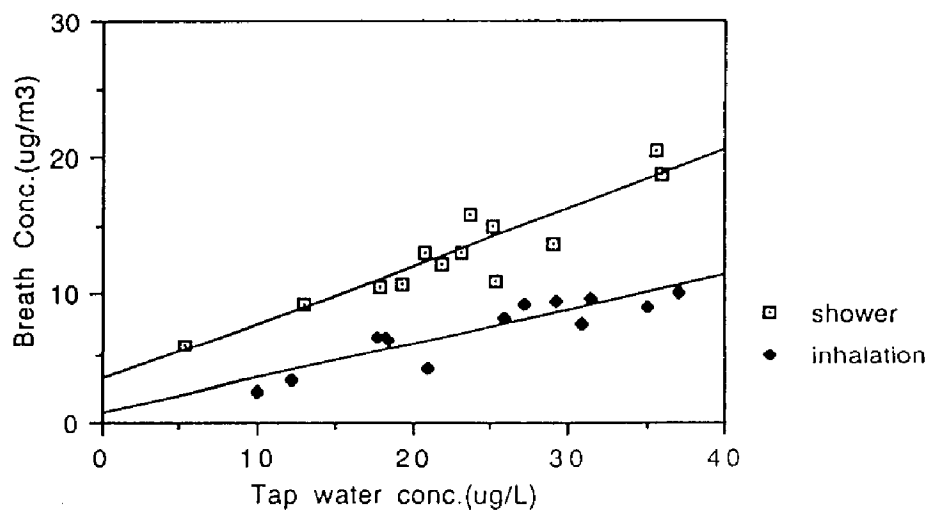


Figure 2. Chloroform breath concentration after normal showers and inhalation only shower versus tap water concentration

Biomarkers and Pharmacokinetics

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Monitoring of biomarkers is a promising technique to help assess both the exposure and dose to critical target sites of toxic chemicals. Biomarkers can range from body burden to antibodies able to detect, separate, and quantify specific adducts formed when toxic chemicals interact with endogenous proteins. To properly interpret the data so that assessments can be made an understanding of the pharmacokinetics of the biomarker is required. Several examples are presented here to illustrate how monitoring and pharmacokinetic information might be integrated to assess dose and exposure.

Acknowledgment: Although the research described in this paper has been supported by the United States Environmental Protection Agency, it has not been subjected to Agency review and therefore does not necessarily reflect the views of the Agency and no official endorsement should be inferred.

INTRODUCTION

Biomarkers of exposure can be defined as any detectable measure or evidence of previous or ongoing absorption of a foreign substance into the body. Examples would include the body burden of the chemical itself or one of its metabolites, any products resulting from the interaction of the chemical and /or its metabolites with endogenous molecules, and any alterations in normal physiologic and biochemical processes. For the markers to be of use in quantitative exposure assessments several necessary criteria must be fulfilled. First, a suitable detection and measurement method needs to be available. The method must allow for accurate measurement at all the expected exposure regimens and levels. Also, a quantitative relationship between exposure levels and the levels of measured biomarker must exist. The choice of the actual biomarker will depend upon many factors including on the specific definition of dose used in the specific case of interest.

In addition, several other characteristics are desirable, and thus should also be sought when developing a marker for exposure assessment. The detection and measurement techniques should be at least as sensitive as existing methods used in conventional exposure assessment methods. The monitoring methods and devices should be relatively easy to transport and inexpensive to use. The monitoring protocol should be designed so as to insure minimal discomfort to the subject. The protocol should facilitate the repeated monitoring of multiple subjects. Methods to analyze and interpret the monitoring results are essential for maximizing the value of information gained from biomarker studies. Finally, the usefulness of a marker is greatly enhanced if it can be used both as a marker of exposure and effect.

When embarking on a biomarker program one must first determine what enhancements to the exposure assessment process will be made by their use. As such, it is very useful to determine how many of the general utilities of biomarkers apply to the specific case of interest. One of the most obvious of these utilities is the ability to measure actual dose by using biomarker based techniques. Conventional exposure assessment methodologies only allow for the measurement or estimation of concentration time profiles at the boundary between environment and subject. Thus, from such data dose can be only be inferred. Biomarker data on the other hand are measurements of the amount of chemical having entered the body. From these measurements the dose can be calculated rather than inferred.

Equally obvious is the fact that biomarker based assessments result in a measure of the integrated dose, from all routes or portals of entry into the body. Conventional exposure assessments can only infer dose and even for this, considerable knowledge regarding exposure by each portal of entry is required. It should also be noted that in many cases, with some additional

information it is possible to apportion the aforementioned biomarker based integrated dose to the various portals of entry. Thus, from biomarker data, both the integrated dose and the specific route apportioned dose can be determined.

Still another important utility of the biomarker approach is that, in many cases, dose, and thus previous exposure, can be determined long after the exposure has ceased. In many cases a biomarker may remain in the body, thereby giving evidence of exposures, for weeks after the actual exposure episode has ceased. Adducts formed by some xenobiotics and their metabolic products to hemoglobin for example, will reside in the body for the life of the erythrocyte which, for the human, is over 17 weeks. Such adducts can be monitored and thus provide evidence of exposure and estimates of dose long after the last exposure incident.

One more utility is that, with proper analysis, biomarker information can be used to estimate the dose to critical organs as well as estimating total body dose. Thorough pharmacokinetic information and appropriate biomarker measurements an exposure assessor can estimate the dose to critical tissues during and long after the exposure period. In addition, critical temporal parameters, such as the time necessary to rid the body or organ of the toxic moiety, can be calculated.

Two cornerstones are necessary in order to realize the fullest utility of the biomarker approach. First, there must, as previously mentioned, be suitable detection and measurement devices and methods. Second, there needs to be an extensive description of the pharmacokinetics of the biomarkers of interest. The pharmacokinetics must be described and modeled in a manner that will result in a maximum use of biomarker measurement data for estimating dose and other related parameters of exposure.

Physiologically based pharmacokinetic (PBPK) models, while not the only approach, offer great promise as tools to accomplish the required analysis of biomarker data. Properly formulated and validated they can be used to first describe physiologic kinetics of the biomarkers associated with a particular chemical. Then, after this developmental stage, their output can serve as an analytical tool for estimating the desired parameters from the biomonitored data. It is their use in this second, or analysis stage, that will be illustrated here.

METHODS

This exercise has been formulated solely for illustrative purposes. As such, the biomarker and dose data were essentially manufactured from past experiences and knowledge. Under actual exposure conditions the formulation and validation of the PBPK model could be quite involved and complex. Usually such models are quite data intense. If models and appropriate data are

lacking they must be generated simultaneously with, or even in anticipation of, the biomarker development. As will be illustrated, more than one biomarker and associated analysis tool may be necessary to get accurate estimates for large exposure ranges. If estimates of the exposure ranges are known apriori it may be possible to reduce the number of necessary biomarkers required.

Discussions of actual model formulation procedures will vary according to the specific case and are far beyond the scope of this paper. The same can be said for the mathematical procedures for solving the mass balance equations that compose PBPK models. Suffice it to say that, to date, complicated models are solved numerically rather than analytically. The expanding capacity and speed of computers has enabled the solution of models by what were previously considered to be tedious numerical methods.

Model simulated output is then used with biomonitoring data from subjects to estimate dose. Again, a variety of methods can be used. The most complicated, but perhaps the method affording the most accuracy and resolution between doses, uses the PBPK model itself. Biomonitoring data is taken. The model is repeatedly solved to determine an estimate for dose which results in the best fit of model output to the monitored data. Numerical methods are used to determine what possible dose level could have resulted in the actual monitored values. Given proper numerical methods and appropriate software, confidence values around the estimated dose can be calculated. In this manner the more reliable and accurate monitoring data will result in greater confidence in the final dose estimates.

A contrasting and less computationally intense method involves using the PBPK model to give outputs at several arbitrary dose ranges. The model outputs are then graphed and the resultant graphs can be used as reference graphs from which to estimate dose ranges after biomarker monitoring is performed.

A third approach is a comprise between the first two. For this case model outputs at several dose ranges are put into a computer data bank. An expert system, with access to that data bank, is then employed to compare the monitored data to model simulated outputs and thus give estimates of dose. Such a computer based expert system could be formulated to perform appropriate statistical analyses of multiple data points of the monitored marker.

Each is advantageous under specific conditions. Following is a simple illustration of the second, or graphical approach.

RESULTS

Figures 1 through 3 illustrate the use of pharmacokinetic information to determine dose in one particular exposure scenario. Eight possible dose levels (1-8) are included in this

illustration. Two things are assumed (with apriori knowledge) about the scenario. First it is assumed or known that exposure is still ongoing and second that the plateau or steady state has been reached.

Three different biomarkers have been monitored. Figure 1 shows the profile of marker 1 for the 8 dose levels. The graph shows the marker's concentration with time profile as determined from the pharmacokinetic analyses for the various doses. If the monitored marker level is less than 4.0 a dose range can be established. For example, it can be observed that if the concentration level (Y-axis) of marker 1 is 3.9 then the dose must then be between level 2 and level 3 (value for marker at dose level 2 = 3.0 and at dose level 3 or higher = 4.0). The resolution could then be increased by increasing the number of simulated model outputs within that range.

If the marker level were greater than 4 it would not be possible to discern between dose levels 3 through 8. Figure 2 is the analogous graph for marker 2. Inspection reveals that this marker can discern between doses within the range of the first four dose levels rather than just the first three.

One might wonder why use marker 1 at all when marker 2 is adequate for a wider dose range? It may be that marker 1 is more accurate at lower doses or that it is easier and cheaper to obtain and analyze. Thus it may be the preferred marker for screening or for determining the lower dose levels.

Figure 3 repeats the process but for marker 3 instead. Inspection here reveals that this marker can discern between doses within the range of levels 5 through 8. It also demonstrates that this marker, due to its kinetic profile, is incapable of being used to estimate the lower dose levels.

Next let us look at a case after exposure has ceased. Figure 4 shows the concentration-time profile of a marker both during and after the exposure period. Making the assumption that monitoring is performed, as indicated, during the post exposure period, a value of 1.0 concentration units for marker 1 can be associated with three different doses of the parent chemical. Resolving between doses can be accomplished by knowing the time after exposure when the monitoring occurred.

Often the exact time that exposure ceased is not known. Resolution between doses can be achieved in such cases by measuring other markers as observed in Figure 5. The top panel of Figure 5 shows the measured value of marker 2 (horizontal line). Clearly this level is higher than any level that is reached at dose level 1 and thus such a measured value would rule out dose 1. However marker 2, at this value, cannot discern between the two higher dose levels. The lower panel of Figure 5 shows the measured value of marker 3. This value can only be reached by dose level 3. Thus, if monitoring of markers 1

(Figure 4) and 2 (Figure 5, top) was not sufficient to discern between the possible dose levels, marker 3 would be monitored.

Figure 6 depicts another series of marker determinations that might be used to differentiate between two doses. Again these measurements, as illustrated here, are made after exposure has ceased. In this illustration one calculates the ratio of the concentration of marker 1 to the concentration of marker 2. That calculated ratio is then compared to ratios similarly calculated for the standard curves (curves shown in Figure 6). It can readily be observed from the example that the ratio of the concentration of marker 1 to the concentration of marker 2 is significantly different for the two different doses depicted here. For the case of dose 1 (upper panel of Figure 6) the ratio of the concentration of Marker 1 to the concentration of marker 2 is approximately 2.0. For the case of dose 2 (bottom panel of Figure 6) the value of the ratio is about 0.7.

CONCLUSIONS

Monitoring of biomarkers is a promising method to help assess both exposure and dose. Biomarkers are evidence of dose rather than just exposure and thus can significantly enhance the conventional exposure assessment process. Also, some biomarkers, due to their long life-time within the body, can be used long after exposure has ceased. Therefore, these markers would lend themselves to monitoring persons whose exposure is expected on an in-frequent basis.

The future use of biomarkers will depend upon several factors. Only those markers which are most easily, accurately, and cheaply applicable under field conditions will be practical. Not all markers will be useful at all exposure concentrations. Those that are only able to detect exposure at rather high concentrations may only be useful for monitoring occupationally exposed populations for example. Others, such as receptor based methods will probably be more sensitive than existing analytical methods and thus be applicable even at environmental exposure levels. Some of these, however may lack selectivity and only be able to indicate exposure to classes of compounds rather than specific chemicals. In such cases some knowledge of the possible chemicals that people have possibly been exposed to will greatly help the assessment process. Other markers while both sensitive and selective may be quite expensive to apply, and thus will be used in only in cases of great impact or where other more conventional monitoring techniques do not suffice. Perhaps the single greatest promise for biomarker based exposure assessment is for their utility in assessing exposure to a chemical found in a mixture. Much remains to be done to determine how useful these techniques will be in such cases, but many of the developing markers are chemical, or at least, class specific and the thus with proper development the impact of concomitant exposure can be quantified.

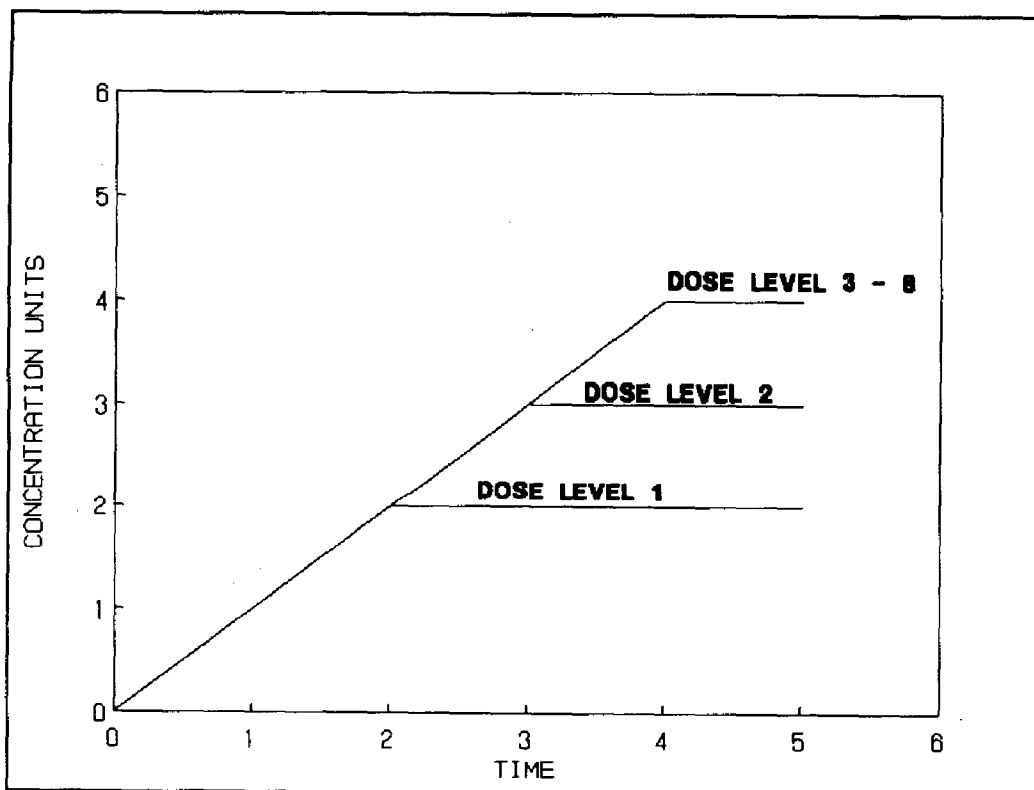


Figure 1. Value of Marker 1 in the body for eight dose levels of a chemical. Time: arbitrary units. Concentration: arbitrary units. Note that the value of the marker is the same for dose levels 3-8.

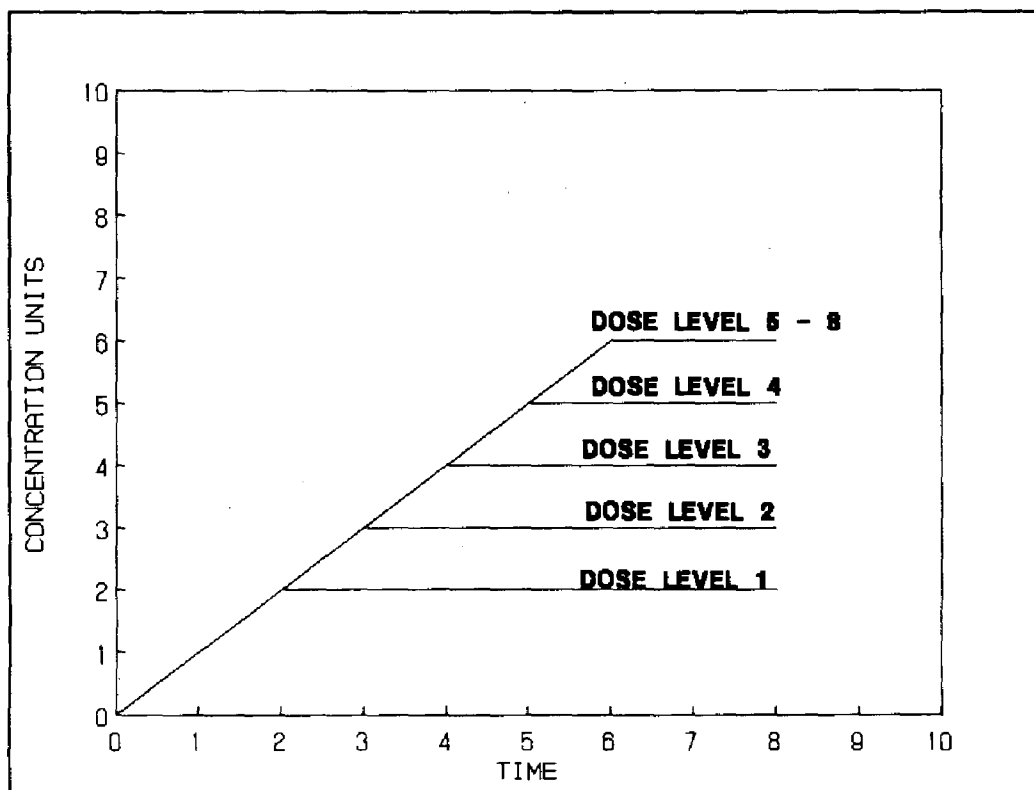


Figure 2. Value of Marker 2 in the body for eight levels of a chemical. Time: arbitrary units. Concentration: arbitrary units. Note that the value of the marker is the same for dose levels 5-8.

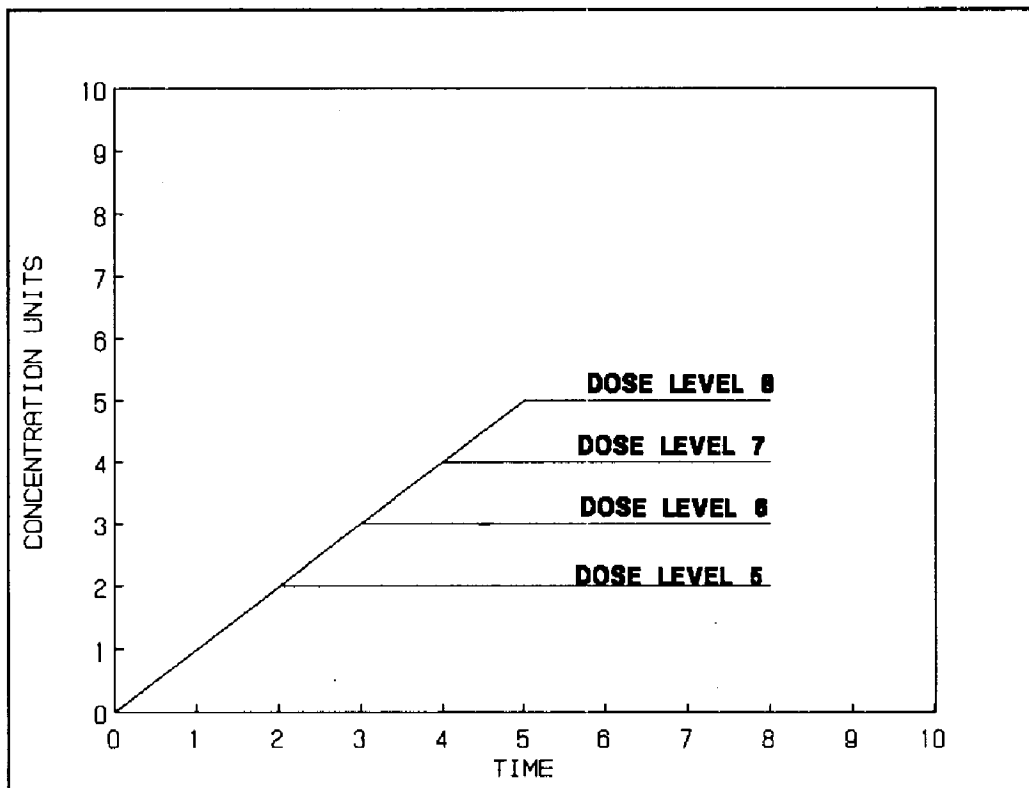


Figure 3. Value of Marker 3 in the body for eight levels of a chemical. Time: arbitrary units. Concentration: arbitrary units.

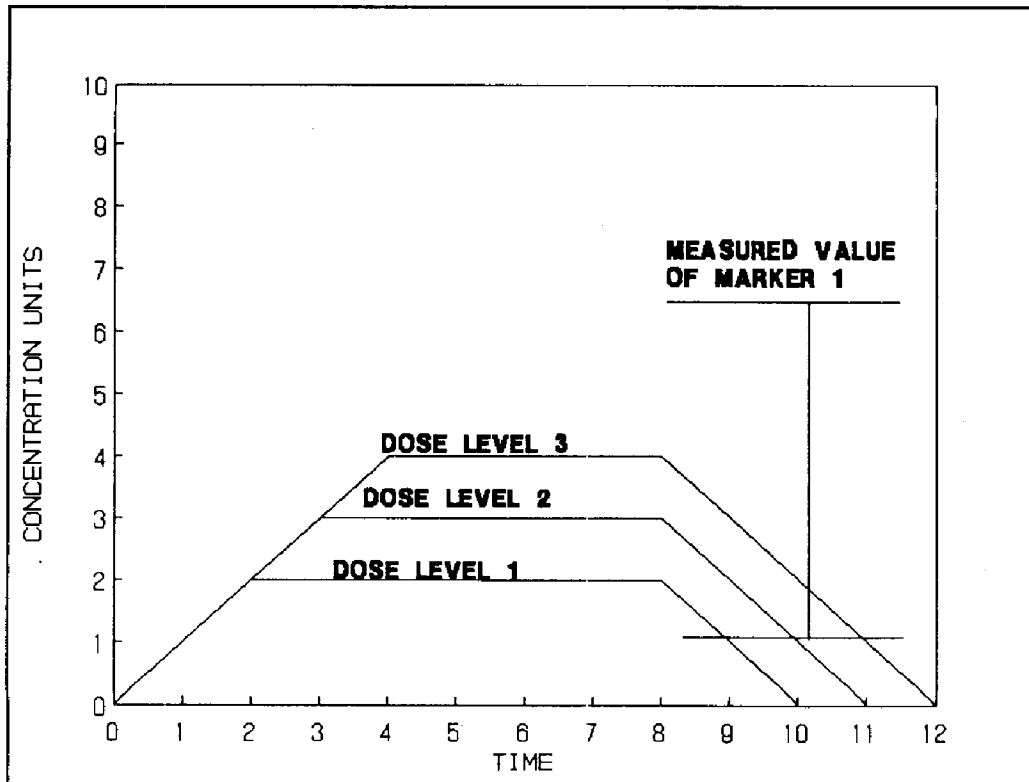


Figure 4. Concentration of Marker 1 at three dose levels: Measured value could be due to any of the three dose levels. Time: arbitrary units. Concentration: arbitrary units.

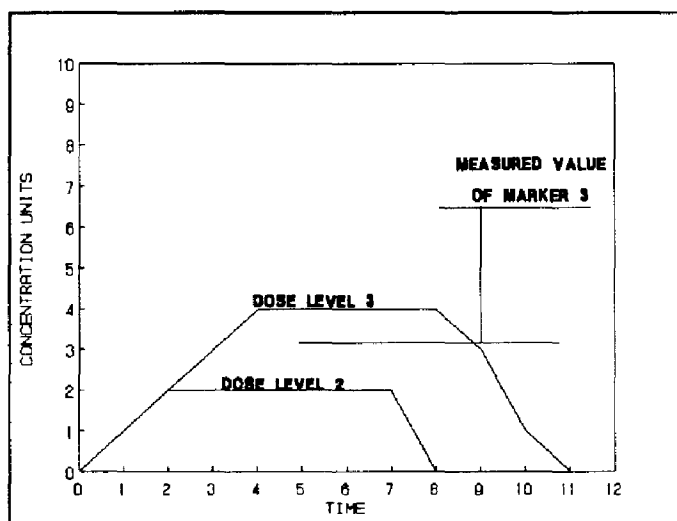
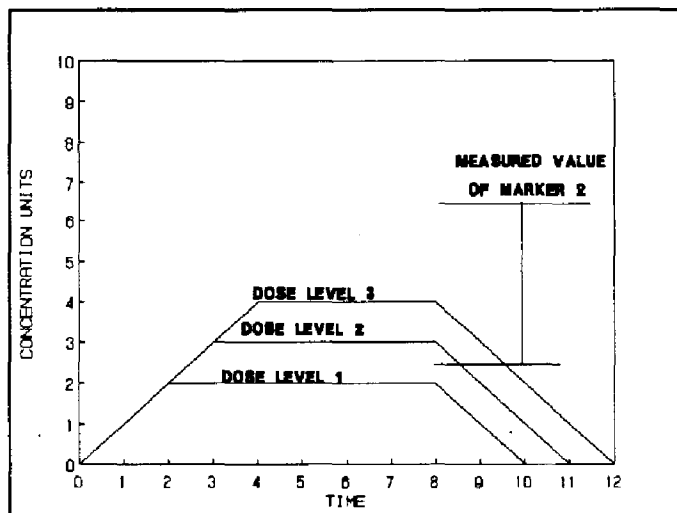


Figure 5
 Measured Values of
 Markers 2 and 3
 Time: Arbitrary Units
 Concentration: Arbitrary Units

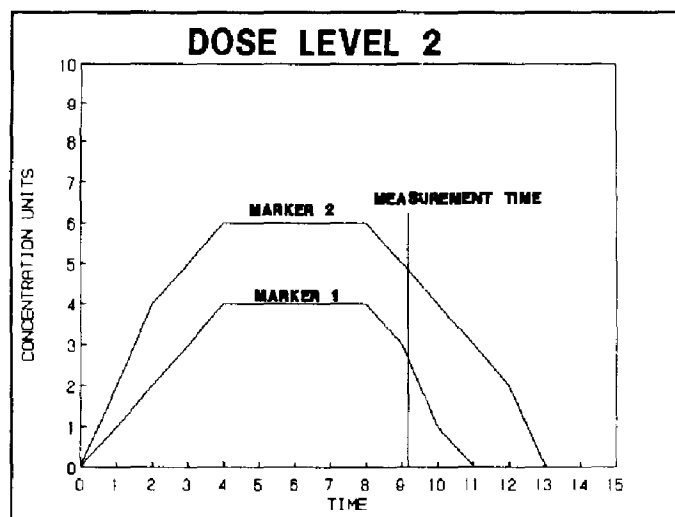
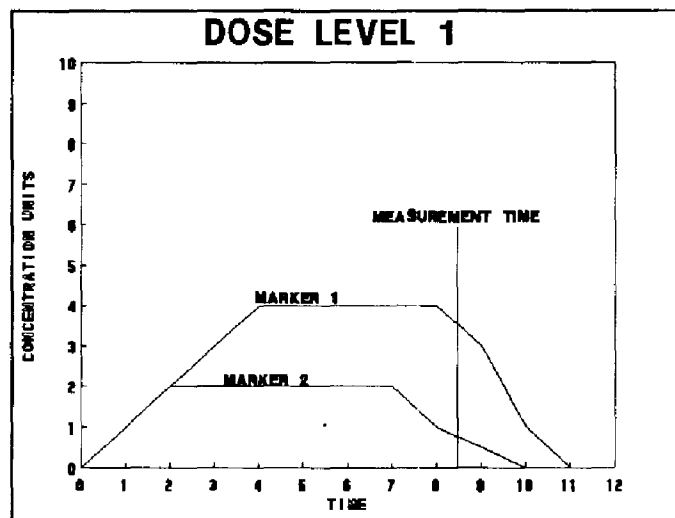


Figure 6

Profiles of Two Biomarkers
 at Two Dose Levels
 Time: Arbitrary Units
 Concentration: Arbitrary Units

REVIEW OF THE PARTICLE TEAM 9 HOME FIELD STUDY

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The 9 home pilot study for the Particle Total Exposure Assessment Methodology (PTEAM) Program has been completed and a population study is being planned for fall 1990. The pilot study was a 9 home field test of instruments, protocols, and sample analysis. The study site was the San Gabriel Valley, CA.

The study logistics were generally successful. Shorter more precise questionnaire material is being developed for a population study. The use of portable microenvironmental samplers could be enhanced by using battery powered samplers. Computer assisted interviewing and data collection was useful for more rapid analysis and cross validation. Data analysis of personal and microenvironmental aerosol samplers has indicated a possible personal cloud (aerosol concentration gradient) effect. This effect is currently being investigated. Elemental analyses have indicated adequate material is collected for XRF.

The PTEAM study is being sponsored by the U.S. EPA and the California Air Resources Board.

Introduction

The U. S. Environmental Protection Agency (U.S. EPA) during the last ten years has begun to assess the importance of human exposure to pollutants as measured by personal and microenvironmental sampling. This summary presents EPA's assessment of the information gathered through a small scale study to assess the design of equipment and survey materials for measuring human exposure to suspended particulate matter.

Classically, exposure to most pollutants was thought to occur when either the individual went outside into a polluted atmosphere or the polluted atmosphere infiltrated into the indoor environment. In the last decade it has been realized that indoor pollutants may be substantially different from outdoor and that indoor pollution may account for the majority of population exposure to many pollutants. Improvement in outdoor ambient air quality and changes in life style, building technology, and the use of chemical agents (pesticides, cleaners, spray propellants, deodorants, etc.) have increased the relative importance of indoor exposure. The average adult spends at least 68-78% of time indoors.

U.S. EPA has conducted a series of field programs to measure distribution of human exposure to volatile organic compounds (Total Exposure Assessment Methodology Program, TEAM), pesticides (Non-Occupational Pesticide Exposure Study, NOPES). The generic TEAM concept seeks to answer fundamental questions regarding the number of persons exposed, the sources of exposure, transport of pollutant to the population at risk, the effects of exposures, the meaning of sampling data in terms of actual exposure, and the estimation of the level of exposure of the actual population to the pollutant in question. The basic ingredients of TEAM study are representative probability sampling, measurement of the pollutant concentrations, measurement of body burden, and recording of each person's daily activities.^{1,2,3}

This document discusses the initial field trial of the Particle TEAM Program. The field study included nine homes and eighteen persons and was concerned with the development and testing of measurement techniques to determine human exposure to aerosols.

The Particle TEAM program seeks to answer questions relating the measurement of aerosol concentration to human exposure. Health related information collected in the Particle TEAM Program will be limited.

The Particle TEAM study objectives are four-fold. The first is to estimate of the frequency distribution of human exposure to particles in the PM₁₀ size range for a metropolitan population. The second objective is to discern the differences among the concentrations of particulate matter measured by personal exposure monitoring, outdoor ambient air sampling, and fixed site or microenvironmental monitoring. The third is the identification of the major sources of exposure and the degree of exposure of an urban population to provide exposure assessment and source apportionment data. The fourth is to develop models for personal exposure and source assessment.

The PTEAM Program seeks to meet the objects through the use of survey design statistics, the physical measurement of the aerosol concentrations in microenvironments where individuals spend time, and by using personal samplers that are carried by the subjects throughout the course of the monitoring. Additionally questionnaires and diaries are used to assess possible routes and sources of exposure to respirable and inhalable particulate matter.

The Particle Total Exposure Assessment Methodology (PTEAM) Program has been developed in three phases. In the first phase monitoring equipment necessary for determining the level of human exposure to aerosols was developed. This included both personal and microenvironmental sampling instruments. The second phase consists of a pilot field program developed to test these instruments in the field. The third and final phase consists of a large field program where a probability design is used to select homes from an urban population. This document concerns some of the results from the first two phases. The third phase is to be implemented Fall of 1990.

From observations made in previous TEAM studies a number of objectives were recognized as necessary in the design of the pre-pilot field program (Phase 2).^{4,5,6} First, adequate testing of methods, protocols, and instruments is needed in the field environment. Questions about logistics of implementation, sampler ruggedness, and suitability had to be answered before the population study. The 9 home field test is the opportunity to insure that the field personnel are adequately trained on all the sampling instruments and protocols and are prepared to interact with the study participants.

Experimental

The study site for the 9 home field test was the San Gabriel Valley, CA. The area was selected for the high levels of both coarse and fine particulate matter found year round in the ambient air.

The components of phase two included preparation of the work plan, site selection, laboratory testing and calibration, development and implementation of sampling design protocols. Two protocols were used in the field test. First a temporal study was performed using five homes, lasting seven days, and including two sets of microenvironmental aerosol monitors within each home. Second, four additional homes were used in a four day spatial study in which three sets of microenvironmental monitors were placed inside each home. A total of eighteen persons, nine homes, nine work places and two central sites were sampled. Methods included microenvironmental and personal aerosol collection of both PM₁₀ and PM_{2.5}. Nicotine was measured using active and passive sampling and associated with both personal and microenvironmental measurements. Radon samples were taken at each of the homes. Air-exchange measurements were also made.

The aerosol sampling equipment used in this study consisted of two types of devices, a personal exposure monitor (PEM) and a fixed location microenvironmental monitor (MEM). The aerosol PEM consists of a flow

controlled personal pump that is worn by the test subject as he/she performs his/her normal daily activities and an inlet and filter pack which are designed to collect particles near the breathing zone. New PEM inlets were designed for Particle TEAM by the University of Minnesota for the measurement of personal exposure to respirable PM_{2.5} or inhalable PM₁₀ particles. Each inlet consists of an impactor classifier to remove particles larger than the predetermined cut size (D₅₀) and to provide a sharp cut (σ_g), and a filter to collect the remaining particles. The inlets were designed to operate with 37mm filters and at 4 LPM.⁷ Both PM₁₀ and PM_{2.5} inlets were evaluated in the 9 home study. The MEM inlets were designed by Marple, Spengler, and Turner to sample at 10 LPM with a sharp cut and had been used in the Harvard Six City Study and others.⁸

Survey questionnaires were developed to screen the population for study selection and to relate activities and sources of aerosol emissions to increased personal exposures. Information areas surveyed include: demographic information (roster of participant household, participant occupation, age, smoking status, sex hobbies, socioeconomic status, housing type), sources of exposures to aerosols and chemical species of interest, activities correlating with exposures, limited health effect or wellness information, ventilation (air exchange rates, heating and air conditioning sources), residence descriptives (e.g., multi-unit, attached), transportation (commuting time, type of vehicle), occupation, and workplace descriptives.

The information was obtained through the use of several different questionnaires and forms administered to the participant and/or completed by technical field personnel. The key survey instruments included a household screening questionnaire, a participant questionnaire, and a 12 hour activity log. The screening questionnaire provides basic demographic information necessary for stratification of the population being sampled. The 9 home study was a purposeful study, participants were selected based specific parameters, such as housing stock, type of employment, and smoking. The participant questionnaire collects data on household characteristics, personal characteristics, and workplace characteristics from the subject. Morning and evening 12 hour activity logs composed of a chronological log and a supplemental close-ended questionnaire were used to provide detailed information on the participants daily activities during monitoring.

Discussion

A series of questions were posed at the outset of the nine home study. These questions were selected to test the ability of the pre-pilot to meet the specific objectives listed above (i.e., testing of methods, protocols, and instruments, logistics, personnel training and interaction). This discussion section presents EPA's assessment of the information gathered through the pre-pilot study to answer some of these questions.

1. Is sufficient PM_{2.5} or PM₁₀ material being collected in a

12 hr period for chemical and physical measurements?

- Do XRF, and/or PIXE have sufficient sensitivity to measure selected elements on 12-hr PM_{2.5} and PM₁₀ collected fractions?
- Are there serious chemical interferences precluding quantitative analysis?

Data collected in the 9 Elemental analysis by XRF indicated that sufficient mass should be obtained for any of the 12-hour sample types to enable high percentage measurable values to be obtained for the most important elements. The exception, however, is Cd. Using the a two-sigma threshold as a quantifiable limit, the reported percent measurable data drop to less than 10%, whether using NEA, Inc. Protocol 9 or 5. Thus, Cd cannot be adequately measured by XRF on PEM and MEM samples in the Pilot Study.

Among the 34 elements, the 13 of primary interest were Fe, Pb, Ni, K, Si, Al, As, Cd, Mn, Se, V, Cr, and Sb. For many of these primary elements, quantifiable concentrations for 100 percent of the analyzed filters were found.

Of the 34 elements listed in these tables, six generally dominated in terms of amount of particulate mass for which they accounted. These were: Si, Ca, S, Fe, Al, and K. For instance, for PEM 10 μ m samples, these six elements accounted, on average, for about 10 percent of the mass, while all 34 together accounted for about 11 percent.

Eight of the PEM filters analyzed by XRF (protocol 9) were analyzed twice (three 2.5 μ m and five 10 μ m samples). For each element, standard deviations and RSDs of the paired concentrations were calculated. Precision was calculated only for those 17 elements exhibiting a high percentage of quantifiable values. Though the sample sizes were obviously small, the results for the different size cuts appeared similar, so the results were combined. Thirteen of the elements had median RSDs between one and ten percent, three elements had RSDs between 10-15%, and one element (P) had a median RSD of 55.7%. Except for P, the precision for the remaining elements (Al, Si, K, Cr, Mn, Fe, Ni, Pb, S, Cl, Ca, Ti, Cu, Zn, Br and Sr) was of acceptable quality.

There appeared to be no serious chemical interferences precluding quantitative analysis. However, the portion of MEM filters that had uneven deposition patterns was examined for elemental non-uniformity. Repeated XRF measurements of the same filter could not identify a problem. However, the method did not allow sufficient room to analyze incongruent areas. An additional examination was performed using duplicate MEM samples with one or both exhibiting bleed. The filters were examined for variability between the duplicate values. Comparing the RSD for 15 duplicates for 14 elements which had measurable concentrations (with those duplicate MEM samples in which neither filter exhibited bleed) did not reveal any obvious differences in variability.

Thirty PEM and MEM filters analyzed by XRF were also subjected to PIXE analysis. In general, when the mean elemental concentration (e.g.

>40 mg/m³) was well above the detection limits, good correlations were observed between the two techniques (e.g., 0.70 to 0.98). For some of the elements, especially for the PEM samples, there appeared to be a difference in the average concentration levels of the two methods, with the XRF usually being higher. This, coupled with the large number of negative concentrations found by PIXE for some elements, suggests that an over-correction of background from blank filters may have occurred for the PIXE-determined concentrations. This interference would be a potential problem in the Pilot study.

2. What is the level of accuracy and precision attainable in PEM and MEM collection for analysis (gravimetric methods)?

a. Precision of PEM Gravimetric Results

Paired PEM samplers carried by the field technicians during pilot (refer to section 5.2) provided some insight into the precision of the PEM method. The RSDs ranged from 1.1-15.0% (median 4.4%) and 4.2-24.8% (median 12.7%) for the PM₁₀ and PM_{2.5} samples, respectively. The precision was deemed acceptable.

b. Precision of MEM Gravimetric Results

Twenty-four pairs of PM₁₀ and PM_{2.5} MEM indoor samples were collected at the participants homes. The RSDs ranged from 0.6-7.4% (median 1.7%) and 0.6-24.4% (median 5.6%) for the 10 μ m and 2.5 μ m samples, respectively. Nine pairs of PM₁₀ outdoor MEM and eleven pairs of PM_{2.5} outdoor MEM samples were collected. The RSDs ranged from 0.8-33.3% (median 3.5%) and 0.6-12.5% (median 2.8%) for the PM₁₀ and PM_{2.5} samples, respectively. It was concluded that the precision was acceptable.

c. Precision of PEM and MEM Filter Weighings

Duplicate weighings for a subset of PEM and MEM filters were performed, thereby allowing an assessment of the precision associated with this portion of the measurement process. The mean RSD for the 10 μ m and 2.5 μ m PEM filter weighings was 1.5% (40 pairs) and 2.65% (19 pairs), respectively. For the 10 μ m and 2.5 μ m MEM filters, the mean RSD was 1.02% (69 pairs) and 1.54% (62 pairs), respectively. The precision for PEM and MEM filter weighings was felt to be acceptable.

d. Precision of SSI Gravimetric Results

The central site data included duplicate SSI PM₁₀ concentrations for each of the 22 time periods of the Pre-pilot Study. The average concentrations ranged from 23 to 149 mg/m³. The relative standard deviations for the 22 pairs ranged from 0.1-23.0% (median 2.9%). This precision was acceptable.

e. Accuracy of PEM and MEM Gravimetric Results Relative to SSI

Two methods were used to estimate a relationships between the central-site PEM and MEM PM₁₀ concentrations and the average of the two SSI PM₁₀ concentrations. One was ordinary least squares (OLS), the other maximum likelihood (ML) estimates. Positive intercepts, which appeared to be of borderline statistical significance, indicated that the PEM-measured concentrations may tend to run slightly higher than the MEM-measured concentrations. On a percentage basis, the estimated difference is smaller for higher concentrations, e.g. about 7% higher when the MEM concentration was 130 mg/m³, and about 24% higher when MEM concentration was 30 mg/m³.

3. What are the difficulties associated with participants carrying the PEMs?

- What is the failure rate and performance record for PEMs?
- What problems are voiced by the participants?

The failure rate for the PEMs was negligible in the field. There was some problem with the repackaging and cracking of the pulsation damping chamber. These problems can and were overcome in the pre-pilot and additional PEM testing. The most significant problem with the PEMs had been the accidental miss-cutting of the 2.5 μ m orifice by MSP, Inc. Twenty-two PM_{2.5} samples were taken with effective cut sizes of 3.9 μ m. These points were tagged in the data base. Debriefing of the participants resulted in no serious complaints in regard to wearing the PEMs. The overall conclusion was the PEMs could be successfully utilized in the Pilot.

4. What are the difficulties associated with placing MEMs in homes?

- Inconveniences to participants?
- Adequately defining locations?
- What is the failure rate and performance record for MEMs?

The majority of problems were encountered during the set-up visit. The most notable problems were space limitations due to the amount of equipment placed in the homes, borderline acceptable noise levels due to the amount and type of equipment placed in the home and the lack of properly grounded power outlets at both inside and outside sampling locations. A combination of improved performance AC powered MEMs to provide quiet indoor sampling and battery powered portable MEMs for outside would solve these problems.

The failure rate for the MEM packages was negligible.

5. Does the Activity Pattern instrument provide usable information for correlation with monitoring data?

- Does the activity recall questionnaire yield adequate response specificity to account/explain the monitoring data?

Is it useful or necessary to know about minor sources and short-term sources when evaluating 12 and 24 hour integrated exposures.

Evaluation of survey instruments included the time activity diary, and time activity diary supplement. The analysis of the time activity and supporting questionnaire data indicated a number of ambiguities and inconsistencies. It was concluded that the response categories in the activity diary were too broad and highly variable to be useful in data analysis and that time indications needed to be clarified. Exposure needs to be better defined, especially in terms of active or passive exposure mode.

Higher MEM concentrations may be the result of home and personal activities. Homes that had the highest indoor MEM2.5 and MEM10 concentrations were later identified to have potential sources of indoor particles (for example, smoking and other dust generating activities, such as cleaning, performing crafts projects). Outdoor activities associated with elevated particulate levels included such activities as sweeping, raking leaves, gardening, and working with horses. More rigorous analysis of the activity data did not result in significant correlations with measured concentrations.

The nicotine data indicated that levels were usually associated with the presence of smokers. Discrepancies between high contact with smokers and low recorded nicotine levels were also evaluated. These data indicated that participants had a hard time distinguishing between smoker contact or exposure and non-exposure. Certainly it appeared that participants could tell when they had direct contact or were within the plume, but they had a lesser ability to distinguish lower levels of contact. In addition, this analysis reconfirmed the statistical analysis of nicotine/time activity and particulate/time activity relationships, where time of reported smoker contact indicated nicotine levels but not particulate levels.

While the field monitoring staff have knowledge which may be beneficial for the accurate completion of the documents, the current survey instrument requires too much time to administer and needs to be reduced in scope and complexity. The time of administration must be reduced, as must the burden of the respondent. Several comments from the respondent debriefing were received concerning the level of detail requested in the diary, and the difficulty in maintaining the document. It was found that information obtained from many questions was not very useful for analysis and such questions should be excluded. In summary, the survey instruments will be redesigned and tested in a focus group setting prior to use in the Pilot Study.

The survey data and analyses provide little hope for correlating minor sources and short term sources when using integrated sampling of 12 and 24 hours. Real time personal sampling methods need to be developed that can more directly tie activity to aerosol particle exposure.

Summary

A number of questions have been posed to be addressed by the PTEAM field study. They fall into four categories: physical sampling, survey/questionnaire, data analysis, and illustrative. Most of the questions have been answered successfully by the 9-home study. The sampling instruments have been shown to work well in the field. Of the total 2240 samples, 99.47% were captured. No significant difficulties were associated with placing fixed location samplers or carrying personal samplers. The level of accuracy and precision was largely resolved. Sufficient PM_{2.5} or PM₁₀ material was collected for gravimetric and elemental analysis on almost all samples taken. Chemical analysis was largely successful.

Disclaimer: This extended abstract does not necessarily reflect EPA policy.

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PARTICLE TOTAL EXPOSURE ASSESSMENT METHODOLOGY (PTEAM):
STATISTICAL ANALYSIS OF SPATIAL AND TEMPORAL PATTERNS

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The Particle Total Exposure Assessment Methodology (PTEAM) Prepilot Study was conducted in the Duarte/Azusa/Glendora, CA area during March of 1989. The study involved personal aerosol monitoring for two participants in each of nine volunteer households, using personal exposure monitors, and particulate monitoring in and near their homes, using microenvironmental monitors. The study's primary purpose was to develop methodology for personal exposure monitoring of particulates, a methodology that could be applied later in a large-scale Pilot Study. In this paper we present some of the statistical results from the Prepilot Study and indicate how such results were used to aid in the design of the large-scale study.

Introduction

In this paper, we examine the spatial and temporal variability of the aerosol concentration data of the PTEAM Prepilot Study conducted in the Duarte/Azusa/Glendora, CA area during March 1989. The study involved personal aerosol monitoring for two participants in each of nine volunteer households, using personal exposure monitors (PEMs), and particulate monitoring in and near their homes, using microenvironmental monitors (MEMs). Time periods of monitoring were of approximately 12 hours duration starting in the evening and in the morning.

Study Design

Primary participants for the PTEAM Prepilot Study were selected from a group of municipal workers who had indicated willingness to participate in the study. Table I summarizes the participant characteristics. Except for the primary participant in house 9, all of the participants were nonsmokers. Table I also indicates the basic structure of the Prepilot design. Monitoring for houses 1 through 5 began on the evening of March 6 and continued for 14 time periods. Starting on the evening of March 16, a second group of homes (Houses 6-9) were monitored for eight periods. PEMs were alternated daily between 10μ and 2.5μ , while both size cuts were simultaneously employed for the MEMs. The MEMs were placed outside of the participants' homes, in the home's main living area (MLA), and in one or two other locations:

House	Main Living Area	Area 1	Area 2
1	Den	Master Bedroom	
2	Kitchen	Master Bedroom	
3	Living Room	Master Bedroom	
4	Living Room	Master Bedroom	
5	Living Room	Bedroom	
6	Den	Master Bedroom	Kitchen
7	Den	Master Bedroom	Kitchen
8	Living Room	Master Bedroom	Study
9	Living Room	Master Bedroom	Dining Room

In some cases, duplicate, collocated MEM samplers were used.

Results and Discussion

PEM Aerosol Concentration Data

The PEM data exhibited a substantial amount of variability, both from person to person and among time periods for a given person. Examination of the data clearly revealed that one major source of such variation was time of day: higher PEM aerosol concentrations generally were observed for the daytime periods. (A similar result holds for the outdoor ambient samples.) Because of the day/night differences, separate statistical analyses were performed for the day and the night periods.

This day/night difference is evident in the Table II results, for instance. This table gives statistics that characterize the distributions of the PEM gravimetric data -- by size cut, time of day, and time of week (weekdays or weekend-days). The statistics reported are the following: the sample size n , which is the number of observations over houses, participants within a house, and time periods; the minimum, maximum, and mean aerosol concentrations (in $\mu\text{g}/\text{m}^3$); the standard deviation (in $\mu\text{g}/\text{m}^3$); and the coefficient of variation (CV), expressed as a percentage. The

mean, standard deviation, and CV for the 17 nonsmoking participants are also shown (the associated n value is one less than that shown for all participants). A similar classification by work-day versus non-work-day, rather than weekday versus weekend-day, was also generated. However, because most of the daytime, weekday samples were associated with periods when study participants went to work (30 of the 33 10μ samples, and 10 of the 11 2.5μ samples), little difference between those results and those depicted in Table II were evident.

Table III indicates the degree to which similar PEM aerosol concentrations for primary and secondary participants were observed. For most houses, the two participants had comparable means and exhibited moderate to high positive correlations. The major exceptions were house 9 and house 6.

The main conclusions about the PEM data that can be drawn from Tables II and III are shown below; analyses of variance (ANOVAs), performed separately by size cut and time of day, tended to support these conclusions.

- Daytime PEM aerosol concentrations, on average, were higher than nighttime concentrations.
- For a given time of day (i.e., day or night), there was substantial variability in aerosol concentrations, both among participants and among time periods within participants. The variability among the daytime aerosol concentrations was generally larger than that among the nighttime observations.
- On average, weekend/weekday (or workday/non-workday) differences in aerosol concentrations, relative to the amount of variation among days within these types, were not large.
- Participants from the same household often (but not always) tended to have comparable levels and similar temporal patterns in their PEM aerosol concentrations.

MEM Aerosol Concentration Data

Table IV shows a temporal summary of the MEM aerosol concentration data from the main living areas of the nine participating households. The table gives the sample size, minimum, maximum, mean, standard deviation, and CV, by size cut, time of week, and time of day. Both daytime and nighttime samples show extensive variation in the concentration levels. However, analyses of variance performed on these data revealed that most of the variation in the daytime samples arose from day-to-day variation within a given house, while for the nighttime samples, when people tended to be at home, there was more variation among houses and somewhat less among days within houses.

A spatial summary of the indoor MEM aerosol concentration data is given in Table V. The table shows means, by indoor location, and correlations among the aerosol concentrations. Sample sizes were 13 or 14 for Houses 1-5 and 7 or 8 for Houses 6-9. Comparable means were usually noted among the various sampler locations within a house, and the correlations among the concentrations from two locations were generally high (median correlation of 0.89 for 10μ samples, and 0.94, for 2.5μ samples).

Table VI shows a temporal summary of the outdoor MEM aerosol concentration data. The table reveals that lower levels tended to occur at night, and that lower and less variable levels occurred on weekend-days, when contrasted with weekdays.

Table VII has two purposes: to provide a spatial summary of the outdoor data, and to furnish a comparison of these data with the indoor MLA data. For each of these two types of samples, the table shows, by house, the mean aerosol concentration ($\mu\text{g}/\text{m}^3$) and the indoor/outdoor correlation. Sample sizes equal 13 or 14 for Houses 1-5 and 7 or 8 for Houses 6-9. ANOVAs applied to the outdoor aerosol data indicated that there was very little house-to-house variability, relative to the day-to-day variation. While the indoor/outdoor correlations were usually positive, they varied widely among houses.

Conclusions

The results presented here demonstrate how the statistical examination of temporal and spatial variability was useful in addressing some of the design issues for the subsequent large-scale study. For example, these analyses were used to draw the following implications for the PTEAM Pilot Study, assuming that similar conditions will be encountered in the study area and time frame chosen for that large-scale study:

- Person-days should be chosen as the basic sampling unit, because of the large temporal variation. Stratification of days by weekend/weekday or work-day/non-work-day is not likely to be very effective in improving precision of estimated PEM gravimetric distributions.
- Because of correlations among PEM concentrations of persons in the same household, the use of multiple persons per household, at the expense of an overall smaller number of households, does not appear warranted.
- If the Pilot Study were to be implemented in the same study area and season that were used in the Prepilot, then the Prepilot data would suggest that the use of outdoor samplers at each house may not be necessary. However, the extent to which similar conditions will prevail in another area and time frame is unknown.
- For some homes and times (but not all), the outdoor aerosol level can be expected to be useful for predicting indoor levels.
- For 12-hour samples, there appears to be little informational benefit to be gained by using multiple MEM samplers placed at various locations within a house.

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TABLE I. SUMMARY OF PTEAM PREPILOT MONITORING DESIGN
AND PARTICIPANT CHARACTERISTICS

House ^b	Participant ^a		Number of Monitoring Periods	No. of Periods at Work	No. Periods with Exposure to Smoking at Work	No. Periods with Smoking at Home	
	Age	Sex				Day	Night
1	P 36	M	14	4	1	0	0
	S 11	M	14	3	0	0	0
2	P 52	M	14	5	5	0	0
	S 49	F	14	0	0	1	0
3	P 32	M	14	5	2	1	0
	S 31	F	14	5	0	0	0
4	P 26	F	14	4	0	0	0
	S 28	M	14	3	1	0	0
5	P 52	M	14	5	0	0	0
	S 24	M	14	1	0	0	0
6	P 32	M	8	2	0	2	1
	S 31	F	8	0	0	1	2
7	P 30	F	8	2	0	0	0
	S 27	M	8	2	0	0	0
8	P 30	F	8	2	2	1	1
	S 11	F	8	0	0	1	1
9 ^c	P 41	F	8	2	2	4	4
	S 18	M	8	3	0	1	3

^aP=primary, S=secondary.

^bAll houses are single family units except numbers 4 and 6.

^cPrimary participant is a smoker.

TABLE II. TEMPORAL SUMMARY OF PEM AEROSOL CONCENTRATIONS ($\mu\text{g}/\text{m}^3$)

Size Cut	Time of Day	Time of Week ^a	All Participants						Omitting Smoker ^b		
			n	Min.	Max.	Mean	Std. Dev.	CV (%)	Mean	Std. Dev.	CV (%)
10 μ	Day	wd	33	66.5	240.9	127.3	43.7	34	126.1	43.8	35
		we	18	59.3	301.9	164.1	70.6	43	156.0	63.6	41
	Night	wd	34	35.4	186.0	87.1	34.0	39	86.6	34.4	40
		we	18	34.4	243.9	93.3	49.9	54	84.4	33.8	40
2.5 μ	Day	wd	11	54.1	240.6	98.0	55.5	57	98.9	58.4	59
		we ^c	15	44.7	219.8	100.2	52.7	53	91.6	42.6	46
	Night	wd	12	28.5	135.7	62.9	37.1	59	56.2	30.6	54
		we	17	19.9	121.2	52.5	27.4	52	48.2	21.6	45

^awd=weekdays, we=weekend-days.

^bValues of n are one less than the n indicated for all participants.

^cTwo "outliers" omitted for this row.

TABLE III. SPATIAL SUMMARY OF PEM AEROSOL CONCENTRATIONS ($\mu\text{g}/\text{m}^3$)

House Number:	1	2	3	4	5	6	7	8	9	Median
10μ Size Cut										
n-Primary	7	8	8	6	6	4	4	4	4	
Secondary	8	8	8	6	6	4	4	4	4	
Mean-Primary	117	100	104	99	77	140	145	116	204	} 113
Secondary	122	110	121	97	86	127	99	165	96	
Correlation of Primary, Secondary ^a	0.63	0.38	0.66	0.63	0.72	0.13	<u>0.99</u>	0.91	<u>0.10</u>	0.63
2.5μ Size Cut										
n-Primary	2	2	2	4	3	4	3	4	4	
Secondary	1	2	1	4	4	4	4	3	4	
Mean-Primary	b	b	b	79	36	74	63	81	142	} 76
Secondary	b	b	b	67	55	78	101	95	53	
Correlation of Primary, Secondary ^a	b	b	b	0.89	0.95	0.59	0.92	<u>0.96</u>	<u>-0.33</u>	0.90

^aCorrelations are based on the smaller n. Minimum and maximum correlations are underlined.

^bInsufficient sample size.

TABLE IV. TEMPORAL SUMMARY OF MEM MAIN-LIVING-AREA AEROSOL CONCENTRATIONS ($\mu\text{g}/\text{m}^3$)

Size Cut	Time of Day	Time of Week	n	Min.	Max.	Mean	Std. Dev.	CV (%)
10 μ	Day	wd	33	21.5	199.9	63.6	33.7	53
		we	18	35.9	169.6	79.8	37.0	46
	Night	wd	32	21.4	169.4	51.3	30.1	59
		we	18	18.9	165.4	57.8	45.7	79
2.5 μ	Day	wd	31	8.3	136.6	37.4	23.6	63
		we	18	20.7	120.0	47.7	23.4	49
	Night	wd	31	13.5	88.5	33.9	19.0	56
		we	18	10.5	144.6	35.0	36.0	103

TABLE V. SPATIAL SUMMARY OF INDOOR MEM AEROSOL CONCENTRATIONS ($\mu\text{g}/\text{m}^3$)

House Number:	1	2	3	4	5	6	7	8	9	Median
<u>10μ Size Cut</u>										
Mean: MLA	41	53	49	47	64	113	57	74	97	} 60
Area 1	40	49	63	47	64	103	41	41	64	
Area 2						92	45	66	93	
Correlation:										
MLA vs Area1	0.89	0.99	0.86	0.97	0.95	0.89	0.70	0.88	0.96	} 0.89
MLA vs Area2						0.99	0.98	0.94	0.83	
Area1 vs 2						0.91	0.77	0.73	0.83	
<u>2.5μ Size Cut</u>										
Mean: MLA	25	37	37	27	41	61	24	32	75	} 35
Area 1	24	33	45	27	41	57	19	25	48	
Area 2						54	20	32	66	
Correlation:										
MLA vs Area1	0.92	0.99	0.95	0.97	0.95	0.97	0.63	0.94	0.94	} 0.94
MLA vs Area2						0.98	0.96	0.97	0.86	
Area1 vs 2						0.94	0.79	0.92	0.91	

TABLE VI. TEMPORAL SUMMARY OF OUTDOOR AEROSOL CONCENTRATIONS ($\mu\text{g}/\text{m}^3$)

Size Cut	Time of Day	Time of Week	n	Min.	Max.	Mean	Std. Dev.	CV (%)
10 μ	Day	wd	32	26.4	144.3	78.2	31.6	40
		we	18	39.5	88.9	61.9	13.8	22
	Night	wd	32	1.8	119.7	56.9	29.1	51
		we	18	25.8	60.0	40.1	10.3	26
2.5 μ	Day	wd	33	9.0	112.3	51.1	29.1	57
		we ^a	18	25.0	61.3	42.1	12.6	30
	Night	wd	33	18.3	116.9	43.2	24.5	57
		we	18	13.6	43.5	26.4	10.9	41

TABLE VII. SPATIAL COMPARISON OF OUTDOOR AND INDOOR AEROSOL CONCENTRATIONS ($\mu\text{g}/\text{m}^3$)

House Number:	1	2	3	4	5	6	7	8	9
<u>10μ Size Cut</u>									
Mean-Outdoor	69	63	68	65	75	48	53	44	46
MLA	41	53	49	47	64	113	57	74	97
Corr. Outdoor & MLA	0.67	0.78	0.79	0.63	0.84	-0.64	0.11	0.79	0.51
<u>2.5μ Size Cut</u>									
Mean-Outdoor	52	49	46	43	52	25	31	30	33
MLA	25	37	37	27	41	61	24	32	75
Corr. Outdoor & MLA	0.75	0.87	0.92	0.77	0.89	-0.21	0.31	0.74	0.26

MEASUREMENTS OF OZONE EXPOSURES

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ABSTRACT

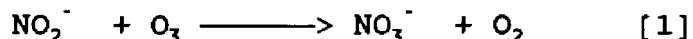
Recently, a personal sampling device was designed to measure human exposures to ozone. This sampler, which is not sensitive to other oxidants, is a filter pack containing a coated glass fiber filter. The coating solution is a mixture of inorganic salts, including nitrite ion. During sampling, ozone oxidizes nitrite to form nitrate. Sampling flow can range between 0.1 and 1.5 Lmin⁻¹. Ozone concentration is determined from the amount of nitrate, measured using ion chromatography. Results from laboratory and field tests suggest a good agreement between measurements made with the filter pack and with a UV-photometric ozone analyzer.

INTRODUCTION

Ozone is an atmospheric oxidant formed through photochemical reactions of volatile organic compounds and nitrogen oxides. Although a great deal of effort has been made to decrease emissions of ozone precursors, ambient concentrations of ozone have only decreased approximately 10% over the last decade [1]. Daily maximum 1-hour ozone concentrations can range between 50 and 300 ppb, and often exceed the ozone National Ambient Air Quality Standard of 120 ppb. For these ambient levels ozone can cause respiratory health effects including changes in lung capacity, flow resistance, and epithelial permeability [2]. While there is a great deal of information about outdoor ozone concentrations, very little is known about indoor concentrations. However, there is some evidence that a large fraction of outdoor ozone penetrates indoors [3]. The development of personal or microenvironmental ozone samplers, can enhance our understanding of human exposures to this harmful air pollutant. This paper discusses the development and evaluation of such sampling methods.

OZONE SAMPLER

The sampler consists of a filter pack and a small pump. The filter pack contains a nitrite-coated glass fiber filter. The coating solution is potassium and sodium salts of nitrite and carbonate with glycerol. During sampling ozone oxidizes nitrite to form nitrate:



Since the above reaction is pH dependent and its rate constant increases with the pH, Na_2CO_3 is used to keep the collecting media alkaline. Also, since the oxidation of nitrite by hydrogen peroxide is fast only at low pH, this sampling technique is insensitive to the presence of hydrogen peroxide which is also an important oxidant.

Optimum collection efficiency is obtained when the nitrite and carbonate in the coating have sodium as the cation for one and potassium for the other. Results from collection efficiency tests showed that ozone reacts with nitrite only when the nitrite and carbonate come from salts of different metals. This may be explained by the fact that the mixed potassium/sodium crystals formed on glass fibers are more hygroscopic. Increasing the number of water molecules at the surface of the crystals enhances the oxidation reaction of nitrite by ozone. For this reason we also include a hygroscopic compound, glycerol, in the coating solution. Thus we speculate that the reaction between the ozone and the coating material occurs through homogeneous aqueous reactions which take place inside microscopic droplets.

After sample collection, the glass fiber filter is transferred to a 7.5-ml polyethylene bottle. Subsequently, 3ml of deionized distilled water is added. The nitrate in this extract is measured using ion chromatography. Since the number of moles of ozone collected on the filter media is equal to the number of moles of nitrate formed, see reaction [1], the air concentrations of ozone are calculated from the nitrate concentrations. Of course nitric acid gas and nitrate particles are collected simultaneously on the alkaline filter media during ozone sampling. However, under usual ambient conditions this positive interference represents less than 5% of the nitrate formed during the nitrite/ozone reaction. Furthermore, reaction of ozone with organic aerosols collected on the filter media can result in the underestimation of ozone concentration. However, due to the amount of nitrite coating on the filter relative to the organic aerosols, this interference is also expected to be small.

The performance of the designed sampler was tested in laboratory and field tests. For the laboratory tests known amounts of ozone, ranging between 50 and 300 μg , were generated using an ozone calibrator. Sampling periods varied between 1 and 12 hours. Figure 1 compares the measurements made with the filter pack and with a UV-photometric ozone analyzer. The ozone masses collected by the filter pack were slightly lower (approximately 9%), than those generated by the ozone calibrator. However, the results of these eight laboratory tests still show a good agreement between the two methods. Considering that a number of other oxidant species could interfere with the ozone measurements, a good laboratory agreement does not necessarily qualify the designed sampler for ambient monitoring. Therefore, the laboratory experiments were followed by field tests. Two filter packs were co-located with a UV-photometric ozone analyzer. Sampling durations were approximately 24 hours. Figure 2 compares the ozone concentrations obtained from the filter pack method and the continuous ozone monitor. Again ozone measurements from the continuous instrument are slightly higher, approximately 5%; however this agreement is considered to be very satisfactory.

Further laboratory and outdoor experiments were conducted at the U.S. EPA laboratories at Research Triangle Park, NC, during the period of February 28 through March 28, 1990. The results are given in Table 1. For the laboratory experiments, the exposure time was 16 hours. Relative humidity varied between <10 and 60%. For one of the chamber experiments, nitrogen dioxide was mixed with ozone to investigate interferences of this oxidant with ozone measurements. For all laboratory tests, as shown by Table 1, a good agreement was found between the continuous U.V. analyzer and the newly-developed ozone sampler. The relative difference between these two methods was less than 10%. Furthermore, although only one outdoor experiment was conducted, the results of Table 1 suggest again a good agreement between the two methods. The observed difference was -9%.

In conclusion, although the results from the above laboratory and field comparison tests are limited, they strongly suggest that the above technique can be used to determine ambient ozone concentrations. More ambient tests must be conducted (different locations and seasons) for a better evaluation of the method. Finally, based on this limited number of data from the preliminary tests we estimate an approximate precision of 9%. Most of this variation was found to be associated with the blank variation. For the future tests we will use filter coating with low nitrate contamination.

DISCLAIMER: This paper has been reviewed in accordance with the United States Environmental Protection Agency's peer review and administrative review policies and approved for presentation and publication.

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Table 1: Results from evaluation tests conducted at the U.S. EPA

Test Type	Relative Humidity	Exposure Time (min)	U.V. analyzer ppb of O ₃	New method ppb of O ₃	Difference (%)
chamber	<10%	960	125.0	117.0	-7
"	<10%	960	37.0	31.5	-5
"	<10%*	960	30.0	30.8	+1
"	35%	960	34.0	32.2	-5
"	60%	960	37.0	39.1	+6
"	<10%	960	15.5	15.9	+3
"	<10%	960	162.0	164.0	+1
"	<10%	960	167.0	168.8	+1
"	<10%	960	150.0	156.9	+5
outdoor	outdoor	1260	31.0	28.3	-9

* In the presence of 76 ppb of NO₂.

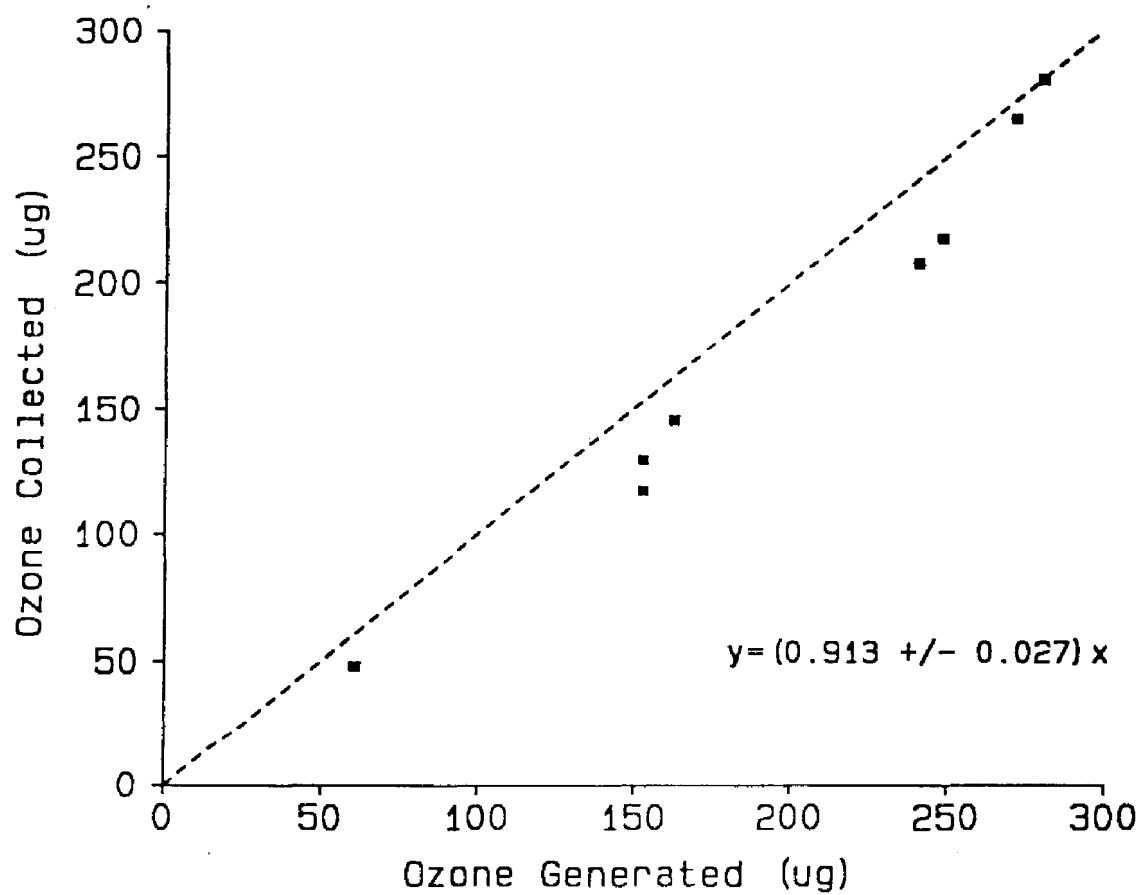


Figure 1: Ozone Laboratory Experiment

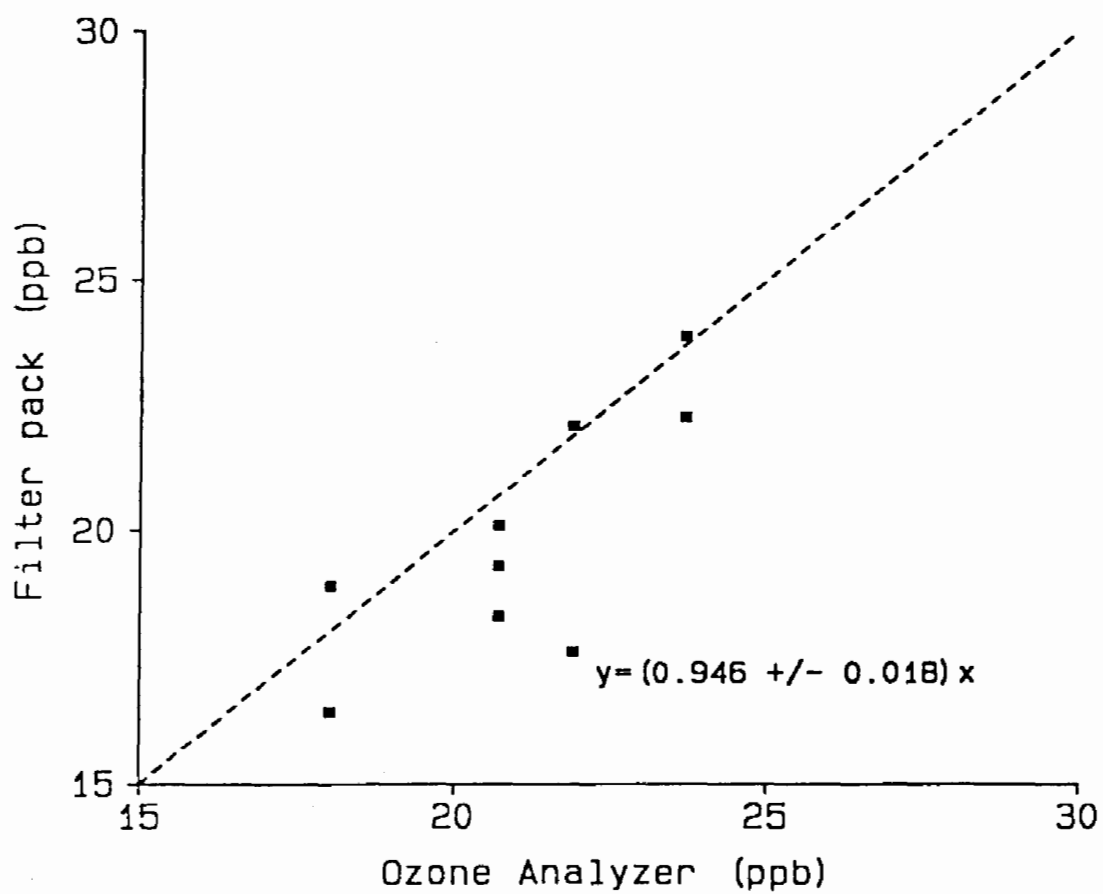


Figure 2: Ozone Ambient Experiment

A PERSONAL EXPOSURE MONITOR FOR CO AND OZONE

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A real-time personal exposure monitor/datalogger for nitrogen dioxide has been adapted to the measurement of ambient concentrations of carbon monoxide and ozone. Selective detection of CO at 0.1 ppm levels has been achieved by the careful selection of sensors, the use of an automatic zeroing technique, and the use of selective chemical filters. The sensitivity and stability of sensors for low CO concentrations has been empirically related to the temperature coefficient of the baseline (no-sample) signal.

Ozone can be detected by the same sensor that is used for nitrogen dioxide. Selectivity is conferred by chemical filters which remove >95% of ozone and <5% of nitrogen dioxide. Critical to achieving sensitivity to ozone is the structure and individual selection of sensors, the development of a selective chemical filter, and the partial replacement of reactive plastics with Teflon. Depending on the sensor, detection limits of 35-150 ppb have been achieved.

Introduction

New discoveries in any field often follow the introduction of new techniques or equipment. It is our purpose to develop instruments that facilitate the study of indoor air pollution, in the hope that it will lead to new understanding of subtle pathological effects. We have developed a real-time monitor and datalogger for very low concentrations of nitrogen dioxide, and we have been working to adapt the same equipment to other injurious gases (1). In this paper, we describe our progress toward the low-level measurement of carbon monoxide and ozone.

Carbon monoxide is a difficult gas to measure in real time in the ambient (0 - 2 ppm) range. Infrared measurement is subject to interferences, and for all standard real-time methods, the equipment is expensive and fragile, and requires expert operators. There are excellent methods for measuring ozone at part-per-billion and even part-per-trillion levels, but again, the equipment is fragile and costly. Both gases are excellent analytes for amperometric electrochemical detection, however.

There are many excellent reasons for choosing amperometric detection. These sensors use virtually no power and are mechanically rugged, which suits them to portable instruments. Since the materials of construction are inexpensive, there is no practical lower limit to their cost; disposable sensors are a near-term possibility. We have already successfully overcome many of the major technical obstacles to ppb-level detection by amperometric methods in our earlier research on nitrogen dioxide. These obstacles, and our responses to them, are outlined in Table I.

Table I. Practical and inherent problems with sub-ppm amperometric detection, and how to deal with them.

Problem	Solutions
-----	-----
Output currents in nanoamps	High-performance op amps, metal film resistors, etc. Careful circuit layout
Inherent noise	Active filtering of signal Signal averaging Very pure sensor materials and clean construction practices
Baseline drift (temp. coefficient of baseline)	Autozero: frequent computer controlled zeroing Selection of sensor
Temperature coefficient of span	Diffusion control of sample access Post-measurement data processing
Limited selectivity	Chemically selective filters

Experimental Methods

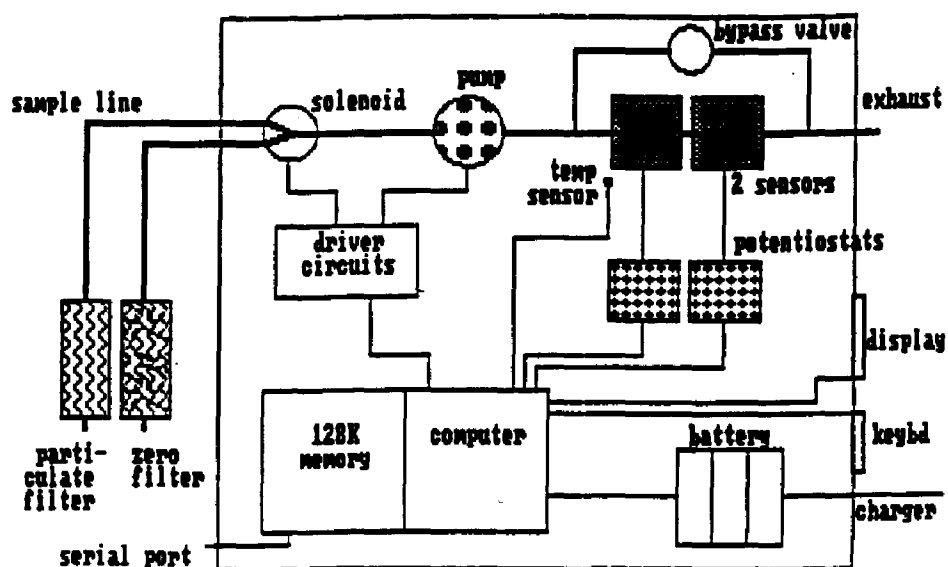
Carbon monoxide dilutions were made from a 334 ppm standard supplied by Matheson Co. A pump and flowmeter were used to dilute the concentrated standard with "zero" air from a cylinder. The diluting air was scrubbed with Purafil, a platinum/alumina catalyst, or potassium palladium sulfite, as described under Results. Purafil is a product of Purafil, Inc., Doraville, GA. Platinum on alumina beads was obtained from Engelhard Corporation, Iselin, NJ. Tubes containing potassium palladium sulfite were made by Kitagawa, Inc. (distributed by Matheson Gas Products).

On-line dilutions of CO were generated by a custom-made diluter, which used Tylan Corp. (Torrance, CA) Model FC-260 mass flow controllers under the control of a personal computer. Any program of dilutions from 1 to 1000-fold could be set up and run on this device.

Ozone was generated with a Thermo Environmental Corp. Model 565 Ozone Calibrator. Clean air from a cylinder is passed through a UV radiation field at 2 L/min, generating ozone concentrations which are adjustable from 0 - 0.5 ppm. Our instrument was calibrated against a Thermo Environmental Corp. Model 560 ozone analyzer provided by J. Woodring of Argonne National Laboratory.

All measurements were made using sensors manufactured by Transducer Research, Inc., installed in a datalogging Personal Exposure Monitor (PEM) instrument developed by TRI for the U.S. Environmental Protection Agency. The PEM is configured according to Figure 1. The incoming sample stream is selected from one of two inlets by a low-power solenoid. Different filters can be installed on the inlets to differentiate among analyte gases. This instrument, and its performance for trace nitrogen dioxide, has been extensively described in an earlier paper (Penrose et al., 1989).

Figure 1. Configuration of the Personal Exposure Monitor.



Results

Carbon Monoxide

Because carbon monoxide was previously considered to be toxic only at high concentrations, there has been little impetus to improve the sensitivity of amperometric CO sensors. When first installed in the PEM, sensors that had passed QA for CO at concentrations of 50-500 ppm were found to drift very badly in the 1-2 ppm range. Reducing the specific surface area of the electrode by using vapor-deposited Pt instead of Pt black is known to be effective in reducing drift. Unfortunately, it is also known to abolish the CO signal (2). As an alternate approach, CO sensors were classified according to the temperature coefficient of their baseline signal. This is a standard part of our testing procedure. A sensor with a near-zero coefficient was installed in the PEM. The response of the baseline output of this sensor with temperature is shown in Figure 2.

In Figure 3 is shown a calibration curve for CO at low concentrations using this configuration, and in Figure 4, a picture of the behavior of the sensor output at the lowest concentrations. The samples were diluted with zero air from a commercial cylinder, and it is immediately obvious that there are several ppb of CO in the cylinder air.

Filters that remove CO are limited. Our standard CO filter is 1% platinum on alumina beads. At room temperature, a column of this catalyst 1.5 cm diam x 12.5 cm long was necessary to remove CO below the 100 ppb level at 400 mL/min. To generate air that we assumed was completely stripped of CO, we passed cylinder air at 40 mL/min through trace CO analysis tubes containing potassium palladium sulfite. Air thus prepared was used to set the "true" zero of the PEM. For routine data collection, we recommended a filter of activated charcoal and Purafil on the sample inlet. This combination removes most organics but not CO. On the zero inlet, we use a 12.5 cm filter of platinum/alumina to scrub CO.

Ozone

Results on ozone are preliminary but very promising. J. Spengler, Harvard University, first alerted us to his observation that our nitrogen dioxide sensor also responded to ozone. In order to selectively measure ozone or NO₂ in the presence of each other, it was necessary to find a chemical filter that efficiently removed one of these gases but not the other. Ozone reacts with nearly all organic chemicals, but we eventually turned up a mixture of organic acids and polyols that absorbed more than 95% of the ozone, while absorbing less than 5% of the nitrogen dioxide. By placing this filter on the zero inlet of the PEM, we can distinguish ozone from interfering gases.

The first experiment was done with the kind cooperation of Dave Halvorson of the DuPont DMT Plant in Wilmington, North Carolina. In Figure 5 is shown the results of our first attempt. At higher concentrations, the signal would not stabilize, but kept rising apparently indefinitely. After the autozero phase, the signal did not start climbing all over again, but took up again where it left off. We interpreted this as scrubbing of the interior of the instrument by the ozone.

Figure 2. For maximum performance, a sensor was chosen that had a minimal baseline shift over the working temperature range.

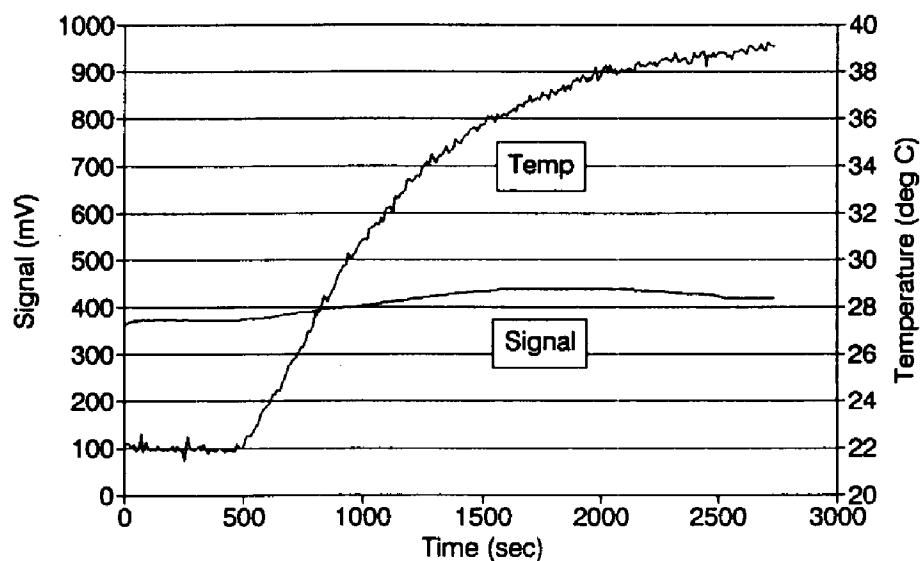


Figure 3. Response of the calibrated instrument to increasing concentrations of CO from an automatic dilution system. The autozero has been turned off.

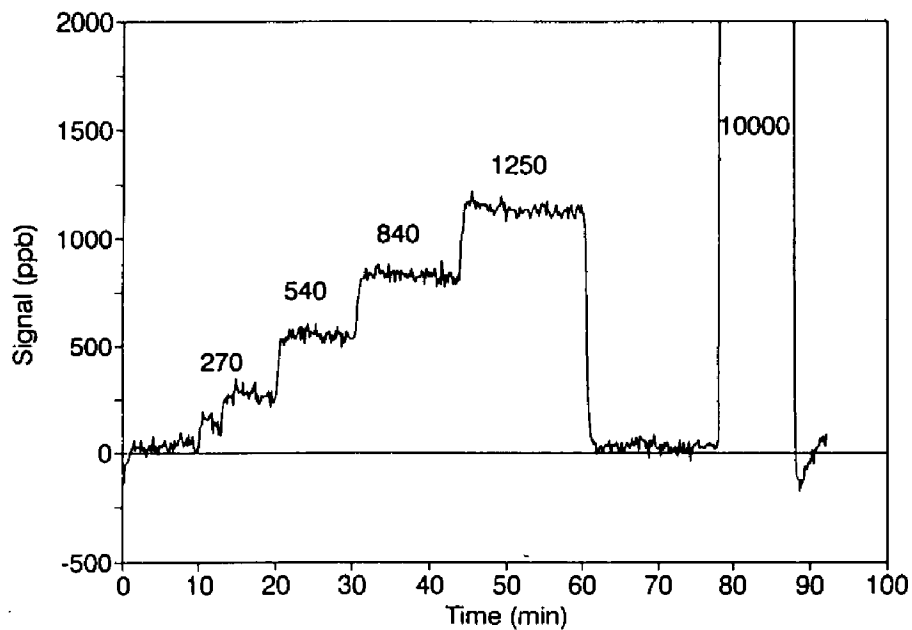


Figure 4. Responses of the PEM to carbon monoxide diluted into laboratory air and cylinder (dry) air. The autozero function has been switched on. The spikes are electronic noise from the switching of the autozero solenoid.

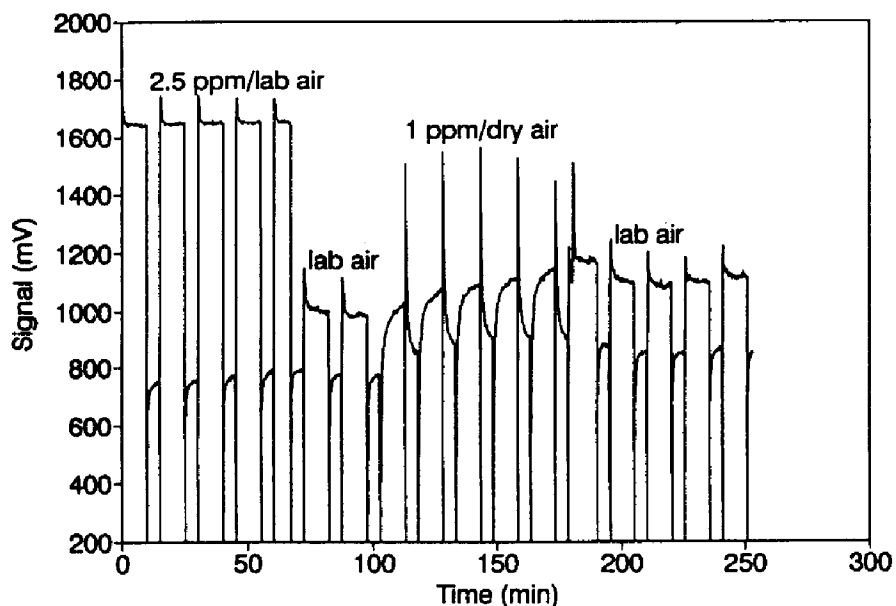
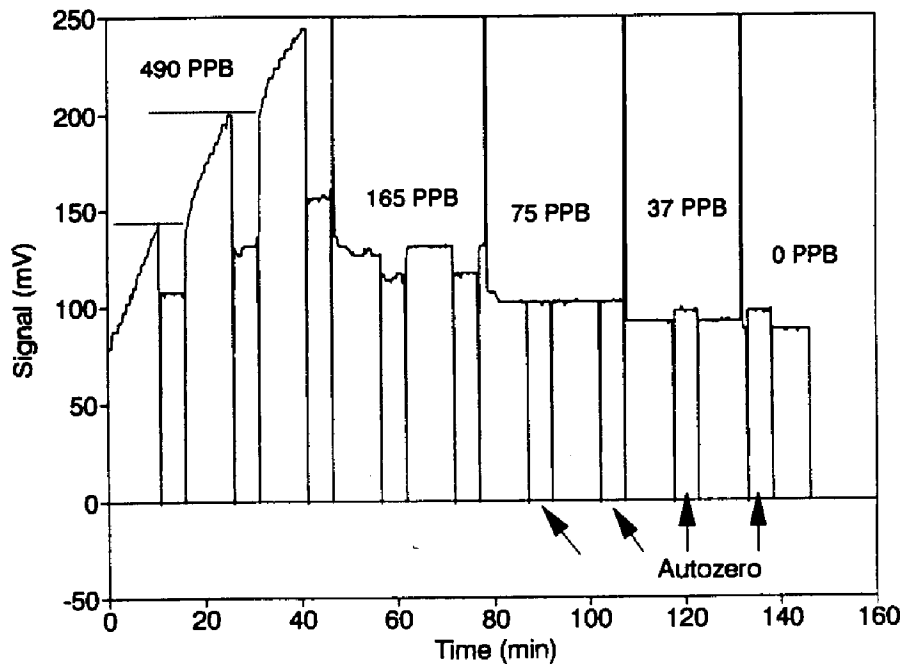


Figure 5. The signal from decreasing concentrations of ozone on a nitrogen dioxide sensor. At high concentrations, an apparent "scrubbing" phenomenon is occurring. Note that the baseline is different for the autozero and the sample measurements.



The gas path of the PEM was made of polyethylene, polypropylene, polyacetal, and polyvinyl chloride; all of these react readily with ozone. Nevertheless, we were able to get a fairly sensitive response to ozone, at least over the region of interest to industrial hygienists. Note that the zero values through the two inlets are not the same. If this offset is applied to the data, the points make a reasonably straight line (Figure 6). This was very encouraging for an initial result.

An interesting feature of the ozone measurements using the autozeroing technique is the very rapid return to zero when the autozero phase begins. This is probably due to the very short lifetime of ozone in the instrument.

We have continued to characterize the ozone response. A variety of nitrogen dioxide sensors have been tested, with variable results (Table II). We have compared the responses of different sensors to NO₂ and ozone concentrations of 500 ppb. The ratios of the ozone-to-NO₂ responses have varied from 0 to 1, that is, some sensors do not respond at all to ozone. From a pragmatic point of view, we can segregate newly-made sensors into ozone responders and non-responders, but it would be valuable to know what manufacturing variables result in ozone-sensitive sensors. This is an area that we are actively pursuing.

Conclusions

(1) Carbon monoxide can be successfully detected at concentrations down to 100 ppb using amperometric sensors.

(2) Sensors with near-zero temperature coefficients for their baseline signal are sufficiently free of drift to use as CO sensors in the ppb range.

(3) Ozone can be measured at concentrations down to 37 ppb, but the responses of sensors are highly individualistic.

Acknowledgments

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Figure 6. The data from Figure 5, corrected for the zero offset.

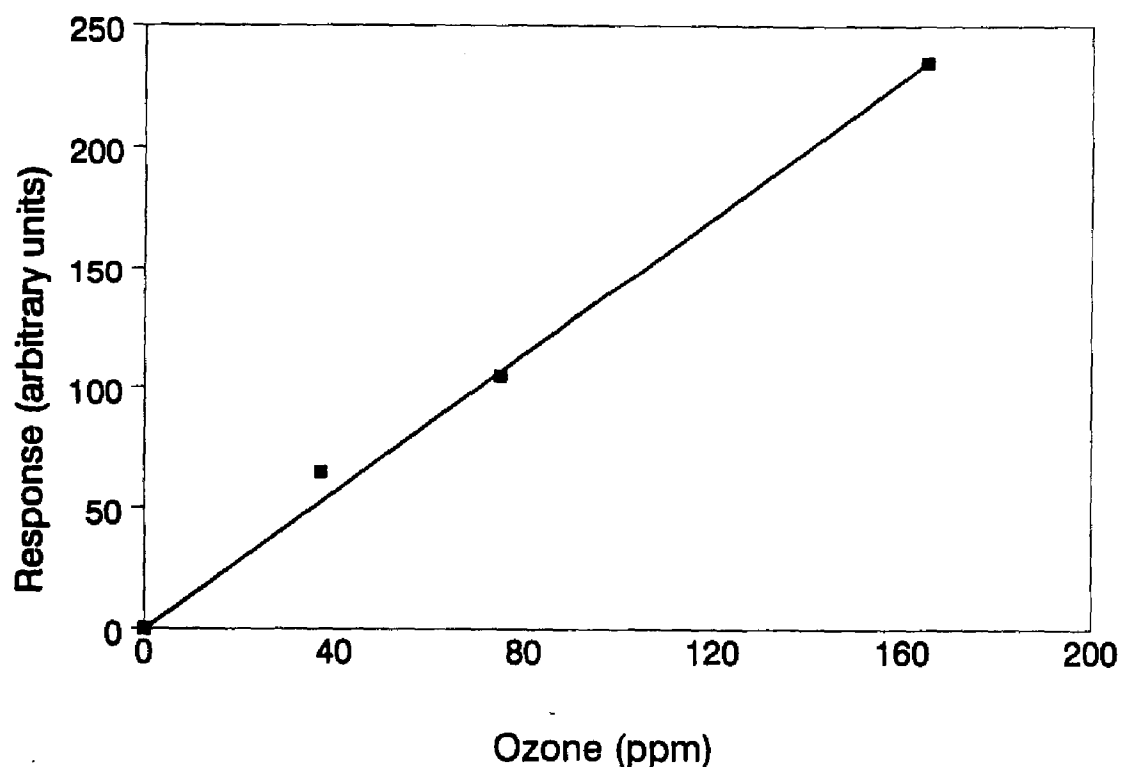


Table II. Relative responses of sensors to nitrogen dioxide and ozone.

Sensor S/N	Response to nitrogen dioxide (nanoamps/ppm)	Response to ozone (nanoamps/ppm)	Ratio O3/NO2
11-21-89-09	46	30	0.65
10337	55	10	0.18
11-21-89-05	50	18	0.36
3-7-90-02	60	50	0.83
3-7-90-03	35	32	0.91
11-21-89-04	not done	0	--

A HEALTH & WELFARE CANADA PROGRAM TO
DEVELOP PERSONAL EXPOSURE MONITORS
FOR AIRBORNE ORGANICS AT $\mu\text{g}/\text{m}^3$

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The objectives, approach and progress in investigations conducted by Health and Welfare Canada to provide suitable personal monitoring methods are discussed. Existing and new, passive and active, sampling procedures were examined for determination of members of several classes of organics. Various sorbents, reagents and devices for collection of the organics and analytical procedures to allow selective and reliable determination over a wide range of concentrations ($0.1 \mu\text{g}/\text{m}^3$ to $500 \text{ mg}/\text{m}^3$; 8 to 24 hr exposures) were evaluated. Sampling tests were conducted over a range of controlled test atmosphere conditions (e.g. temperature, relative humidity, air velocity, co-contaminants) and in the field. Procedures for determination of chlorinated, aliphatic and simple aromatic hydrocarbons were developed and are now available. Methods for selected aldehydes and polycyclic aromatics are at various stages of evaluation and comparison.

Introduction

Current activities at the Environmental Health Directorate of the Department of National Health and Welfare (Canada) include investigations to determine the toxicity and potential human exposure to substances such as polycyclic aromatic hydrocarbons (PAH), aromatic amines (AA), aldehydes, methanol and chlorinated and simple aromatic and aliphatic compounds. Exposure to these organics may arise from their occurrence in indoor air due to human activities and the use of certain materials in buildings or through their presence during the development, production and use of unconventional sources of energy, such as those derived from coal and methanol. The principal objectives of the program are: to assess the hazards to human health associated with indoor air contaminants and those resulting from energy-related initiatives

and developments; and, to make recommendations to minimize potential health hazards.

In recognition of the need to define "acceptable air quality", our Directorate, in collaboration with a Federal-Provincial Working Group on Indoor Air Quality, recently published the "Exposure Guidelines for Residential Air Quality". Also, a protocol for investigation of indoor air quality (IAQ) problems in offices and institutional buildings is in preparation. To complement such guidelines and in response to and anticipation of needs arising from energy-related initiatives, the Directorate is conducting various research studies. The approach and recent progress in the development of personal exposure monitoring methods for several classes of organics are summarized here.

Experimental

Gas chromatographs (GCs) equipped with flame ionization detectors (FIDs) were used for analyses of reagents and extracts from chamber tests and were calibrated daily using standard solutions over the full range of analyte concentrations. Capillary columns (J&W Scientific Inc.) used were DB-WAX for volatile organic compounds (VOCs), aldehydes and methanol and DB-5 for PAH and AA. Confirmatory analyses and analyses of field tests samples were done with a Finnigan Ion Trap Detector (PAH and AA) and with a Hewlett-Packard Mass Selective Detector (VOCs, aldehydes, methanol) installed on Hewlett-Packard model 5890 GCs. Sampling devices are briefly described in the appropriate sections.

Results and Discussion

Traditional integrative sampling methods for area and personal exposure monitoring usually have been based on active sampling techniques. Recently, passive sampling methods relying on diffusion controlled analyte collection have gained some acceptance for use in occupational monitoring of analytes, typically, at mg/m^3 and investigations in this laboratory^{1,2} have demonstrated their usefulness for determination of analytes at ug/m^3 . Although procedures and availability of materials are often well established, some disadvantages of active sampling methods are that they usually require equipment calibration and operation by experienced personnel and are relatively cumbersome, inconvenient and expensive compared to passive methods. There are few validated passive sampling methods, sampling rates must be determined over a range of conditions and the technique is not suitable for particle collection. However, for most volatile organic compounds (VOCs), the technique provides sufficient sensitivity and is attractive due to its convenience and low cost. Therefore, our studies focussed, when practical, on passive methods.

The selection of target compounds was based largely on reports of their occurrence in the environments of concern, assessment of their potential toxicity and consideration for their selective determination together with other members of their group. In addition, the compounds were selected to represent a range of compound types within a class. The selected compounds were: VOCs; n-hexane, n-decane, α -pinene, d-limonene, dichloromethane, chloroform, 1,2-dichloroethane, trichloroethylene, tetrachloroethylene, 1,1,2,2-tetrachloroethane, penta- and hexachloroethanes, benzene, toluene, ethylbenzene, o-, m-, and p-xylenes, styrene,

p-cymene, naphthalene, 1,3,5- and 1,2,4-trimethylbenzenes, m- and p-dichlorobenzenes, and 1,2,4-trichlorobenzene; methanol; aldehydes; formaldehyde, acetaldehyde, acrolein, crotonaldehyde, benzaldehyde; PAH; biphenyl, phenanthrene, benz(a)anthracene, (naphthalene); AA; carbazole, 2-aminobiphenyl, quinoline.

Objectives and conditions for method development were:

Objectives: accuracy, within ± 15 % of reference method; overall precision, < 15 % RSD; collection and extraction efficiencies, each > 75 %; storability of collected analyte on sorbent, 2 weeks with < 10 % loss; passive device sampling rates, $\leq \pm 10$ % over range of evaluation conditions. An additional objective was to use common materials and analytical procedures, where possible, for the various classes of organics.

Evaluation conditions: exposure time-VOCs, 24 hr - aldehydes, methanol, PAH & AA, 8 hr; method detection limit & quantitation concentration range -VOCs & aldehydes, 10 & 50 to 5000 $\mu\text{g}/\text{m}^3$ - methanol, 0.5 & 2.5 to 500 mg/m^3 -PAH & AA, 0.1 & 0.5 to 50 $\mu\text{g}/\text{m}^3$; relative humidity, 10 to 95 %; temperature, 10 to 35 ° C; air velocity at passive sampling device, 0.05 to 1.8 m/sec. Effects of light, pressure, etc. were not considered for these tests.

To determine the reliability of data on airborne contaminants and human exposure, air sampling methods must be evaluated under a wide range of atmospheric conditions. Effects of co-pollutants, temperature, humidity and the physical state of target organics are some of the influences which must be understood. Two test atmosphere generating systems^{3,4} were designed and constructed to provide accurate data on a wide range of controlled conditions which are difficult to obtain in the "field" for sampling tests. A system⁴ which allowed monitoring of artificially generated airborne analyte concentration by gravimetric and on-line GC methods was used for most of the chamber studies on vapour phase organics.

VOCs

The home environment can contribute significantly to the exposure of Canadians to airborne pollutants since they spend a large proportion of their time indoors and apply various energy conservation measures which can adversely effect indoor air quality (IAQ). VOCs, such as chlorinated hydrocarbons, have been identified among indoor, airborne substances which can cause health concerns and require controlled exposure. However, there is a lack of data on the occurrence of airborne VOCs in Canadian homes, partly due to the lack of inexpensive and reliable monitoring methods.

Although five commercially available devices were considered, only the Pro-Tek G-AA (E.I. du Pont de Nemours Co.) and OVM 3500 (3M Co.) monitors were evaluated extensively. The SIS monitor (Scientific Instrumentation Specialists) was tested but was considered too expensive for large surveys; the SKC monitor (SKC Inc., catalog no.530-01) design was judged unsuitable for study objectives; and there was concern with the supply of Abcor GAS-BADGES (Abcor Development Corporation). Tests with 26 target compounds showed recoveries ≥ 75 % for most of the analytes extracted with carbon disulfide from the Pro-Tek and OVM sorbents spiked at levels corresponding to the range of target concentrations. Although included in subsequent tests, naphthalene showed variable and poor recoveries (26 % overall) and its determination by use of these charcoal based sorbents was considered semiquantitative. Difficul-

ties with reliable quantitation was observed with some of the VOCs at levels near the method detection limit (MDL). Problems with reliable determination of styrene will be discussed elsewhere⁵.

Chamber tests were conducted with the simultaneous use of charcoal tubes (SKC, 100mg/50mg) and exposure of both types of passive devices at 0.01, 0.5 and 1.8 m/sec air (face) velocity. In summary, no starvation effect was observed at 0.01 m/sec but the Pro-Tek devices showed a significant increase (e.g. > 50 %) in sampling rates (SRs) when the face velocity was increased from 0.5 to 1.8 m/sec and a slight increase (e.g. 10 %) in SRs with analyte concentration and temperature. The Pro-Tek device also showed greater variability of SRs with changing relative humidity (RH) than the OVM monitor. Since the effects of changing chamber conditions were more pronounced with the Pro-Tek devices, only the OVM monitor was evaluated for all target VOCs. Field tests with 10 of the target VOCs showed excellent correlation ($r > 0.95$) between results obtained with the OVM monitors and the charcoal tube (SKC, 400mg/200mg) reference method, the passive method detection limits were 1 to 2 $\mu\text{g}/\text{m}^3$ and the precision for replicate determinations (± 7 to 10 %) was better than for the active method (± 5 to 14 %). Results of studies with exposed monitors suggested that monitors should be analyzed within two weeks since losses of about 20 % of the collected analytes could be expected after three weeks of storage. Since the performance characteristics and reliability of the method based on the OVM 3500 have been defined, a program to monitor the occurrence of ca. 20 of the VOCs in Canadian homes is scheduled to begin this year and after completion of a pilot study to aid in establishment of the survey protocol. Meanwhile work will continue on evaluation of a recently developed miniature passive sampler using in situ extraction and analysis⁶.

Aldehydes and methanol

The development of personal exposure monitoring methods (PEM) for airborne aldehydes and alcohols resulting from the use of vehicles fueled by neat alcohol and alcohol blends was identified as a high priority. As determined in reviews of the literature, there are no suitable and/or validated methods for accurate determination of personal exposure to airborne aldehydes⁷ and methanol at the concentrations and conditions of concern.

Development of suitable active and passive methods has been slow due to problems with standard atmosphere generation, method blanks, recovery efficiencies, selectivity and other concerns. Derivatization during collection was chosen since this potentially provides better selectivity, sensitivity and storability than collection of underivatized aldehydes. After evaluation of several reagents, 2,4-dinitrophenylhydrazine (DNPH) was chosen for impregnation of glass fibre filters subsequently placed into empty OVM monitors (passive) and two stage, 37 mm filter cassettes (active) and impregnation of XAD sorbent in Supelco ORBO-43 tubes (active) or placed into OVM monitors (passive) and SKC monitors (passive). A large number of chamber tests showed that the impregnated ORBO-43 tubes provided results similar to those for the T05 reference method⁸ adapted to GC analysis. Cassette samplers (active) demonstrated analyte capacity limitations, reproducibility was poor for the SKC samplers, there were discrepancies in calculated sampling rates between passive samplers and acrolein and crotonaldehyde exhibited low values for both active and passive samplers. Experi-

ments were conducted, with some success, to find a suitable wetting agent, e.g. glycerol, to cope with low recoveries at low humidity. Presumably due to the reactive nature of aldehydes, particularly the unsaturated compounds, it was difficult to ascertain the true concentrations in the chamber by the gravimetric, on-line GC or T05 methods. Recently completed investigations suggest that the passive method using OVM monitors can meet the stated objectives as effectively as the active methods. However, the effects of co-pollutants, e.g. ozone, and other factors on the collected analytes remain to be determined.

Initial evaluation of candidate sampling methods for methanol showed that extraction with carbon disulfide gave low recoveries (ca. 30 %) with Pro-Tek G-AA and OVM 3500 sorbents and that NIOSH method no.2000 (150mg/150mg silica gel) was inadequate at the target concentration range. Subsequently a variety of sorbents (silica gel, Carbosieve, charcoal cloth, granular charcoal, OVM sorbent) and extraction solvents (deionized water, butanol in carbon disulfide, chloroform, etc.) were examined and preferred candidates were chosen. Several chamber tests using large silica gel tubes (700mg/150mg/150mg) for the reference method and OVM 3500 and charcoal cloth in empty OVM monitors for passive sampling have been completed and show promising results.

PAH & AA

A critical literature review⁹ and a limited monitoring study¹⁰ emphasized the lack of suitable methods for reliable determination of personal exposure to PAH and AA but provided guidance for methods development and evaluation studies. Subsequently, active sampling methods for particulate and vapour phase PAH and AA were developed and evaluated^{11,12,13} and studies are continuing with use of a special test atmosphere system³.

Development of a passive monitoring method for vapour phase compounds has required extensive investigations to provide reliable and accurately characterized test atmospheres and to find suitable sorbents, extraction solvents and monitor design and to develop sensitive analytical techniques. Current investigations suggest that the use of ORBO-43 in OVM monitors may provide a suitable sampling method. However, evaluation of candidate methods in test atmospheres may not be completed due to a lack of resources.

Conclusions

Passive sampling methods for target VOCs, aldehydes and methanol were characterized and the reliability determined for the range of conditions defined under study objectives. An initial objective was achieved in part for the VOCs, aldehydes and methanol by the common use of DB-WAX columns and the OVM 3500 monitor housing. Instances of significant effects of atmospheric conditions were identified. It is quite possible that some of the observed effects are due to physical changes (e.g. dried sorbent, wet membrane) in sampler structure.

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NEW DERMAL EXPOSURE SAMPLING TECHNIQUE

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A ring of polyurethane foam (PUF ring) on a stainless steel roller (PUF roller) is designed to simulate a young child's dermal exposure as it is pulled over a sampling surface. This is an economical and consistent sampling device which always applies constant weight on the sampling surface. We found there is no statistically significant difference between the recovery of any of 13 pesticide residues from aluminum foil by this sampling device as it rolls over these residues and by dermal pressing on these residues with the human hand heel.

INTRODUCTION

Young children may receive substantial exposure to pesticide residues on indoor surfaces and in house dust, especially during the crawling and early walking stages. A sampling instrument is needed which reliably reflects the exposure of young children to prevalent pesticides on indoor surfaces. In our opinion, the sampling instrument should meet two requirements. First, the absorbent used by the sampling instrument should have similar pesticide absorption efficiency as the human skin. Secondly, the sampling instrument, while collecting pesticides from the sampling surface, should apply constant pressure on the surface which is similar to that of a toddler while crawling or walking. In addition, the dermal sampling area should be easily measured.

The PUF roller sampler, which consists of a ring of polyurethane foam (PUF ring) on a stainless steel roller (Figure 1), is designed to simulate the dermal exposure of a crawling or walking toddler as it rolls over a sampling surface.

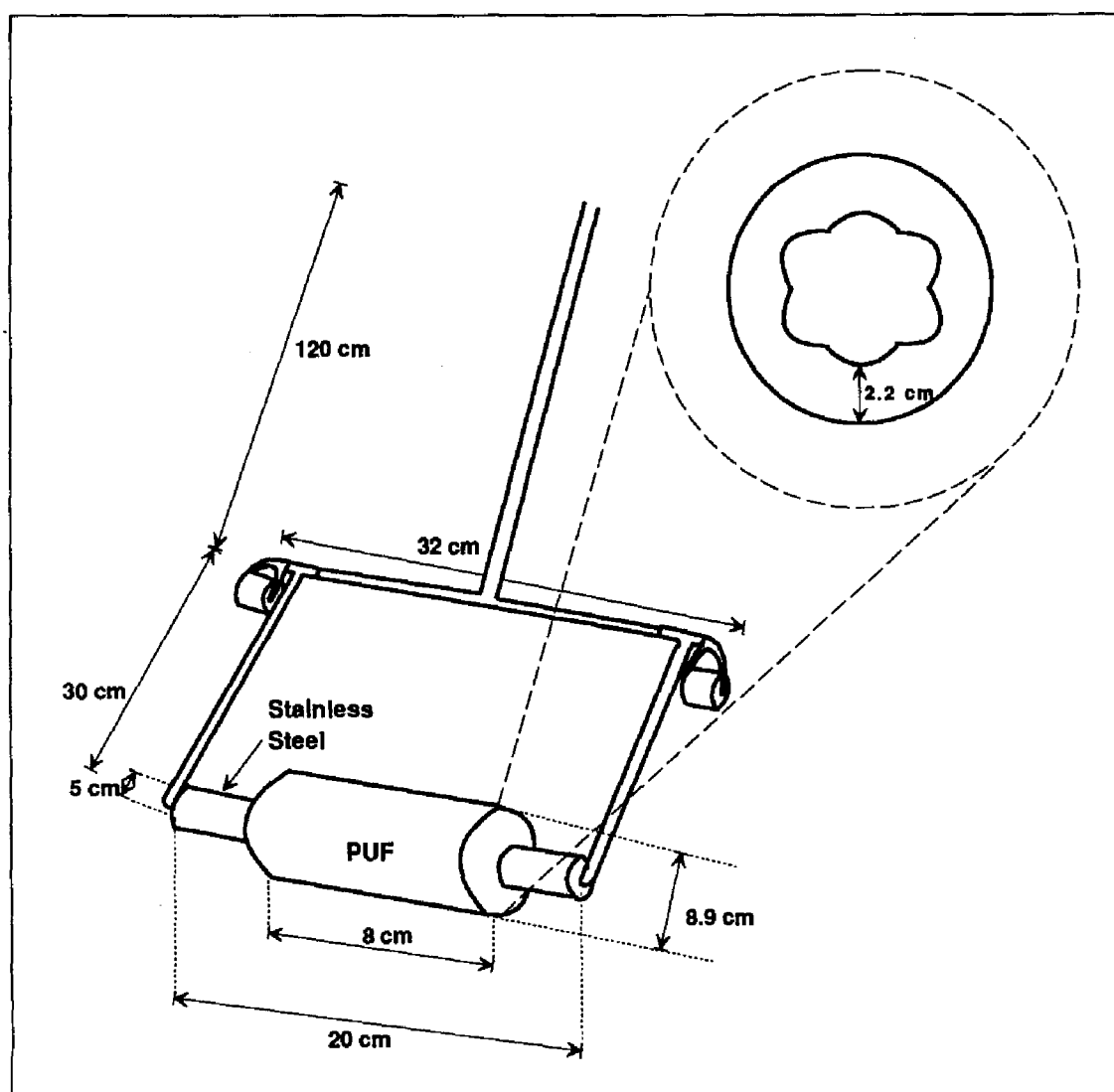


Figure 1. Schematic of PUF Roller Sampler

The stainless steel roller provides constant pressure on a sampling surface through the PUF ring as it rolls, because the pulling or pushing force of the person holding the PUF roller arm will only be applied to the wheel, and not to the freely rotating roller axis. The sampling area rolled over by the PUF ring is also easily measured. However, how does the PUF roller compare with human skin in respect to collection of pesticides from the sampling surface? In this study, we compare the PUF roller with the human heel by rolling the PUF ring over, or pressing hand heel on, dry pesticide-spiked spots on an aluminum foil surface. The percentages of pesticides collected by these two techniques will be compared and discussed. The usage of the aluminum foil avoids the complexity of other sampling surfaces. The pesticides used in the experiment are listed in Table I. These pesticides were selected because they are frequently found in residential house dust and represent the major pesticide structural classes.

TABLE I. PESTICIDE EVAPORATIVE LOSS FROM ALUMINUM FOIL SURFACE^a

Spiked Pesticides	Percent Recovery			
	Test 1	Test 2	Test 3	Mean Recovery
<i>ortho</i> -Phenylphenol	61	101	101	88
Propoxur	85	136	130	117
Diazinon	82	115	113	103
Carbaryl	78	217	53	116
Heptachlor	83	98	104	95
Aldrin	80	98	104	94
Chlorpyrifos	82	102	107	97
γ -Chlordane	86	103	108	99
α -Chlordane	87	103	108	99
<i>p,p'</i> -DDE	87	105	111	101
Dieldrin	87	104	109	100
Methoxychlor	102	105	113	107
Permethrin	111	106	110	109

a Last spiked residue spot allowed to dry for 90 seconds before spiked foil squares are placed in Soxhlet extractor.

EXPERIMENTAL

Analytical Procedure

Four of the spiked pesticides (*o*-phenylphenol, propoxur, diazinon and carbaryl) are analyzed by gas chromatography/mass spectrometry (GC/MS). Gas chromatography with electron capture detection (GC/ECD) and GC/MS are used as the primary and secondary analytical methods, respectively, for the other spiked pesticides. Since 2-propanol is used to wash the 13 target pesticides (Table I) from the human hand heel in this study, all injection standards for both quantitation methods are prepared in 2-propanol. The internal standard quantitation method is used for GC/MS analyses, while the external standard method is used for GC/ECD analyses.¹

Aluminum Foil Sampling Surface Preparation

A new 120 cm × 30 cm dry acetone-washed aluminum foil strip is used for each test involving the hand press, PUF roller, or surface pesticide evaporation loss. A total of 250 µl of a 400 µg/ml standard solution containing all the compounds in Table I is spiked onto the aluminum foil surface, by using a 250-µl syringe to uniformly transfer 25 µl of the solution to the center of each of ten 10-cm sections of foil from 1 cm above the surface. Each application takes approximately 5 sec. Using this procedure, each spike was observed to dry in a circular disk (radius about 1.3 cm) on the aluminum foil surface in about 75 sec. All the tests involving the PUF roller, hand press and pesticide evaporative loss from the aluminum foil surface commence 90 sec after the last spike is applied and are conducted in the same laboratory location (24.3-25.1°C at 50.5% relative humidity). This standardizes the amount of pesticides left on the aluminum foil after the 90-sec drying period in each test.

Dermal Sampling by Hand Heel Press

Two subjects, one with dry hands and the other with moist hands, perform the hand press recovery tests. The subject washes his hands with soap and water approximately 5 min before each test. For the first hand press recovery test, the subject presses the heel of the hand (beneath little finger to above wrist) over each dry circular spiked disk on the aluminum foil surface for about 1 sec in a 90° rolling motion (from hand perpendicular to surface to hand flat on surface) at a pressure of about 1 lb/in². After pressing the same hand heel over the remaining nine spiked spots on the aluminum foil surface, the hand is immediately rinsed by squirting 20 ml of 2-propanol from a Teflon® squeeze bottle over the hand heel, with the rinsate passing through a collection funnel into a vial. The collection funnel is rinsed with 10 ml of 2-propanol into the vial. The 30-ml hand rinsate is then concentrated to 2 ml and split for GC/ECD and GC/MS analysis. Each subject performed a second rinse of his hand heel with 2-propanol after the first hand press test. The second rinsate is collected into a different vial, concentrated and analyzed as before. The second rinsing monitors whether any pesticides remain on the hand heel of each subject.

Two different hand motions were also studied. For the second hand press test, all procedures are the same as the first test except the hand heel rests on each pesticide-spiked disk for 5 sec. For the third hand press test, the only difference is to slide the hand heel over each spiked disk.

PUF Roller Pesticide Recovery

The PUF roller sampler has an exchangeable stainless steel roller. A PUF with 8.9 cm OD and 8 cm length is cut in the center to form a ring with the dimensions shown in Figure 1. After cleaning by consecutive Soxhlet extraction with acetone and with 6% ether/hexane, this PUF ring is carefully slid onto the stainless steel roller with a dry hexane-washed Teflon® sheet between the stainless steel roller and the PUF ring. The function of the Teflon® sheet is to ease the PUF in sliding on and off the roller.

This study is designed to simulate the dermal exposure of a one-year old toddler to pesticide residues on a hard surface. The stainless steel roller of the PUF roller used in this experiment weighs 3.38 kg, which exerts a surface pressure of $(3.38 \text{ kg} \times 9.8 \text{ m/sec}^2)/(0.080 \text{ m} \times 0.057 \text{ m}) = 7300 \text{ Pa}$ while rolling over a surface. A crawling, 20-lb child will support his weight with two hands (each approximately 2 in. by 3 in.) and two knees (each approximately 2 in. by 2 in.). The surface pressure when crawling is $20 \text{ lb}/(2 \times 6 \text{ in}^2 + 2 \times 4 \text{ in}^2) = 1.0 \text{ lb/in}^2 = 6900 \text{ Pa}$. When walking, the child's weight is supported on two feet (each approximately

2 in. \times 4 in.), and the surface pressure is $20 \text{ lb}/(2 \times 8 \text{ in}^2) = 1.25 \text{ lb/in}^2 = 8,600 \text{ Pa}$. Hence the PUF roller used in this study applies the same range of pressure as a one-year child when crawling or walking.

To collect a sample, the PUF roller sampler is pulled once over a spiked aluminum foil strip at a speed of 10 cm/sec. After a single pass, the PUF ring is carefully pulled away from the roller using forceps. The forceps are then rinsed with 6% ethyl ether in hexane. The PUF ring along with the rinsate is placed in a Soxhlet extractor. The PUF ring is then extracted with 6% ethyl ether in hexane for 18 h and the final extract concentrated to 2 ml for both GC/MS and GC/ECD analysis.

Pesticide Evaporative Loss from Aluminum Foil Surface

The pesticides in hexane are spiked on the aluminum foil surface and the solvent evaporated to leave pesticide residue spots. Experiments were performed to evaluate the loss of pesticides due to evaporation during the 90-sec drying time.

Ten 4 cm \times 4 cm dry acetone-cleaned squares of aluminum foil are placed on a 120 cm \times 30 cm aluminum foil strip and each aluminum square spiked from 1 cm above surface, with 25 μl of a 400 $\mu\text{g/ml}$ standard solution containing all the compounds in Table I, allowing 5 sec to apply each spike. The ten squares are collected in a Soxhlet extractor 90 sec after application of the last spike and extracted with 6% ethyl ether in hexane for 18 h. The extract is concentrated to 2 ml and split equally for GC/ECD and GC/MS analysis. This pesticide evaporative loss experiment is performed three times in the same manner.

Extraction Efficiency of Pesticides from PUF Ring

Two clean PUF rings are each spiked with 250 μl of the 400 $\mu\text{g/ml}$ standard solution in hexane containing each compound in Table I. Each PUF ring is then Soxhlet extracted separately with 6% ethyl ether in hexane for 18 h and each extract concentrated to 2 ml and split equally for GC/ECD and GC/MS analysis.

RESULTS AND DISCUSSION

The analytical results of the pesticide evaporative loss from the aluminum foil surface are shown in Table I. There is almost no loss of each pesticide from the aluminum foil surface 90 sec after the last spiking. Therefore, no correction is made for the evaporative loss of any pesticide from the aluminum foil surface. Table II demonstrates good extraction recovery for all the pesticides from the PUF ring. Thus no correction for extraction efficiency is made either.

After the first hand press test, each human subject rinses his hand heel twice. For each pesticide, the ratio of the amount recovered in the first rinsing divided by the corresponding total amount recovered in both rinsings is shown in Table III. It is clear that almost all pesticides are recovered in the first rinsing.

**TABLE II. EXTRACTION EFFICIENCY OF PESTICIDE
FROM PUF RING**

Spiked Pesticides	Spiked Amount (µg)	Percent Recovery		
		Test 1	Test 2	Mean Recovery
<i>ortho</i> -Phenylphenol	100	70	95	83
Propoxur	100	89	162	126
Diazinon	100	90	127	94
Carbaryl	100	84	144	114
Heptachlor	100	92	99	96
Aldrin	100	88	99	94
Chlorpyrifos	100	90	101	96
γ-Chlordane	100	94	100	97
α-Chlordane	100	95	101	98
p,p'-DDE	100	96	103	100
Dieldrin	100	96	102	99
Methoxychlor	100	102	105	104
Permethrin	100	108	103	106

**TABLE III. EFFICIENCY OF ISOPROPANOL RINSE OF
HAND HEEL AFTER HAND HEEL PRESS**

Spiked Pesticides	Percent Rinse Efficiency ^a	
	Subject 1	Subject 2
<i>ortho</i> -Phenylphenol	88	100
Propoxur	79	99
Diazinon	90	98
Carbaryl	82	99
Heptachlor	96	99
Aldrin	97	99
Chlorpyrifos	97	99
γ-Chlordane	98	99
α-Chlordane	98	99
p,p'-DDE	98	100
Dieldrin	98	99
Methoxychlor	97	99
Permethrin	98	99

$$a. \text{ Efficiency (\%)} = \frac{\text{First Rinse Recovery}}{\text{First Rinse Recovery} + \text{Second Rinse Recovery}}$$

The three replicate results of the PUF roller recoveries of the pesticides spiked on an aluminum foil strip after pulling the PUF roller once over the spots are shown in Table IV. In general, the three recoveries of each pesticide are consistent in the replicate tests. The mean recovery of each pesticide is between 5 to 9% with a relative standard deviation less than 32%. An extra test was performed in which the PUF roller jammed after rolling over seven spiked spots and slid over the remaining three spots. Table IV shows the recoveries were at least

double in this test. Therefore, sliding the PUF roller instead of just rolling over the pesticide spiked spots will increase the pesticide recovery substantially.

TABLE IV. PUF ROLLER PESTICIDE RECOVERY^a

Spiked Pesticides	Percent Recovery ^b					Recovery Roller Slide Test ^c
	Test 1	Test 2	Test 3	Recovery		
				Mean	Std Dev	
ortho-Phenylphenol	5.2	7.8	10	7.7	2.4	16
Propoxur	5.9	9.7	7.9	7.8	1.9	29
Diazinon	5.4	6.9	7.2	6.5	1.0	20
Carbaryl	3.8	5.9	6.4	5.4	1.4	33
Heptachlor	7.0	8.0	8.5	7.8	0.8	18
Aldrin	7.6	7.6	8.5	7.9	0.5	18
Chlorpyrifos	5.5	6.9	8.8	7.1	1.7	17
γ-Chlordane	7.9	6.8	8.7	7.8	1.0	18
α-Chlordane	7.6	6.9	8.4	7.6	0.8	18
p,p'-DDE	8.0	7.5	9.4	8.3	1.0	21
Dieldrin	6.6	6.6	8.4	7.2	1.0	18
Methoxychlor	11	6.6	8.9	8.8	2.2	18
Permethrin	7.7	6.7	9.2	7.9	1.3	18

a The PUF roller exerted a pressure of 7300 Pa when rolling over the foil surface.

b The PUF roller rolled over 10 spots (total 100 μ g for each pesticide) at 10 cm apart at a speed of 10 cm per second.

c The roller accidentally jammed after rolling over 7 of the 10 residue spots and slid over the remaining 3 spots.

The hand heel press recovery of pesticides by both dry and moist hands using three different hand motion over the ten dry pesticide residue spots are shown in Tables V and VI, respectively. The mean pesticide recoveries were between 5 to 16%, with larger variation than recoveries by the PUF roller. This larger variation may be due to the different types of hand heel presses applied. The pesticide recoveries of the dry and moist hand heel roll presses with 1 sec duration have similar values. The pesticide recovery of the dry hand press for 5 sec has similar recovery as that of the 1 sec roll press, but the dry hand slide collects more of the less volatile pesticides than either of the other dry hand press motions. The moist hand press for 5 sec collects more of the less volatile pesticides than the 1 sec roll press by the same hand. However, the moist hand has more friction while sliding over residues on the aluminum foil surface which causes the moist hand to skip. The moist hand skipping may cause the lower pesticide recovery than the dry hand obtained in the hand press slide. These data suggest that the hand heel roll is more reproducible between subjects than other hand press motions.

TABLE V. HAND HEEL PRESS RECOVERY OF PESTICIDES BY DRY HAND USING THREE HAND MOTIONS OVER TEN DRIED SPIKED PESTICIDE SPOTS

Spiked Pesticides	Percent Recovery by Hand Heel Motion ^a				
	1s Heel Press	5s Heel Press	Heel Slide	Subject 1	
				Mean	Std Dev
<i>ortho</i> -Phenylphenol	8.4	13	9.7	10.4	2.4
Propoxur	5.4	4.2	6.5	5.4	1.2
Diazinon	6.4	5.6	7.0	6.3	0.7
Carbaryl	9.3	7.7	11	9.3	1.7
Heptachlor	9.5	9.0	8.6	9.0	0.5
Aldrin	9.5	9.3	10.0	9.6	0.4
Chlorpyrifos	7.7	6.4	9.1	7.7	1.4
γ -Chlordane	8.6	6.6	9.8	8.3	1.6
α -Chlordane	8.6	6.8	11	8.8	2.1
p,p'-DDE	8.6	7.2	12	9.3	2.5
Dieldrin	8.8	6.7	11	8.8	2.2
Methoxychlor	6.7	8.5	16	10	4.9
Permethrin	6.4	7.4	20	11.2	7.6

a All motions at hand heel pressure on foil of about 1 lb/sq in. (7000 Pa).

TABLE VI. HAND HEEL PRESS RECOVERY OF PESTICIDE BY MOIST HAND USING THREE HAND MOTIONS OVER TEN DRIED SPIKED PESTICIDE SPOTS

Spiked Pesticides	Percent Recovery by Hand Heel Motion ^a				
	1s Heel Press	5s Heel Press	Heel Slide ^b	Subject 2	
				Mean	Std Dev
<i>ortho</i> -Phenylphenol	10.3	8.0	6.3	8.2	2.0
Propoxur	7.2	5.4	3.9	5.5	1.7
Diazinon	9.8	9.8	4.9	8.2	2.8
Carbaryl	9.6	7.2	4.6	7.1	2.5
Heptachlor	10	13	5.6	9.5	3.7
Aldrin	9.9	14	6.8	10.2	3.6
Chlorpyrifos	8.9	11	6.1	8.7	2.5
γ -Chlordane	9.3	13	6.7	9.7	3.2
α -Chlordane	9.3	13	7.4	9.9	2.8
p,p'-DDE	9.2	14	8.3	10.5	3.1
Dieldrin	9.4	13	7.3	9.9	2.9
Methoxychlor	8.5	22	8.5	13.0	7.8
Permethrin	7.8	22	17	15.6	7.2

a All motions at hand heel pressure on foil of about 1 lb/sq in. (7000 Pa).

b Hand heel observed to skip while sliding over residue spots on aluminum foil.

The null hypothesis of no difference in mean contact recovery between the PUF roller and the hand press was evaluated against the two-sided alternative for each pesticide by the two-sample t-test at the 0.05 significance level. All hand press recoveries of both subjects were combined since mean dermal recovery did not differ significantly between the subjects for any spiked pesticide. The results shown in Table VII indicate there is no statistically significant difference in mean contact transfer recovery between the PUF roller and the hand press for any of the 13 spiked pesticides.

TABLE VII. COMPARISON OF MEAN CONTACT RECOVERY OF PESTICIDE RESIDUES BY PUF ROLLER AND HAND HEEL PRESS

Spiked Pesticides	Mean Contact Recovery of Residue from Aluminum Foil, Percent		Statistically Significant Difference? ^b (p-value)
	PUF Roller	Hand Press ^a	
ortho-Phenylphenol	7.7	9.3	No
Propoxur	7.8	5.4	No (p=0.055)
Diazinon	6.5	7.2	No
Carbaryl	5.4	8.2	No (p=0.08)
Heptachlor	7.8	9.3	No
Aldrin	7.9	9.9	No
Chlorpyrifos	7.1	8.2	No
γ-Chlordane	7.8	9.0	No
α-Chlordane	7.6	9.4	No
p,p'-DDE	8.3	9.9	No
Dieldrin	7.2	9.4	No
Methoxychlor	8.8	11.7	No
Permethrin	7.9	13.4	No

- a For both subjects, since there was no statistically significant difference in mean dermal contact recovery between subjects for any spiked pesticide.
- b Two sample two-sided t-test of difference in mean recovery at $\alpha=0.05$. p-values of borderline significant differences in parentheses.

This finding suggests that the PUF roller may be an ideal dermal exposure sampling technique. A follow-up study is evaluating the similarity of the PUF roller and hand press in contact transfer recovery of pesticides in carpet-embedded house dust.

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A LOW COST SAMPLER FOR MONITORING WORKER EXPOSURE TO HERBICIDE RESIDUES IN FOREST FIRE SMOKE

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ABSTRACT

Concerns have been raised about worker exposure to herbicide residues in smoke from prescribed fires on herbicide-treated forest sites. Modeling studies have shown that the risk to forest workers is insignificant; however, the models had not been verified under actual field conditions partly because detection devices needed to monitor worker breathing zone smoke concentrations had been unavailable.

We developed a personal monitor and an area monitor which measure concentrations of smoke particulate matter and airborne herbicide residues in the breathing zone of workers who are engaged in normal operations of prescribed forest fires. Both monitors employ 25 mm diameter plastic disposable sampling cassettes which contain a glass fiber filter and polyurethane foam as the collection media. The low cost (approximately \$1.50) of each loaded cassette permits a one-time use and thereby eliminated cross contamination of samples and minimizes logistical problems normally associated with sampler recycling.

The monitors were tested in the laboratory and successfully used on operational prescribed fires at 14 sites in Georgia which had been treated with herbicides at various time intervals prior to burning. No airborne herbicide residues of hexazinone, triclopyr, imazypyr, or picloram were detected (detection range of 0.1-4.0 $\mu\text{g}/\text{m}^3$). Smoke particulate matter concentrations up to 3700 $\mu\text{g}/\text{m}^3$ were detected by the personal monitors and 45,000 $\mu\text{g}/\text{m}^3$ by the area monitors. These field tests confirm earlier models which predict insignificant risk of forest workers to herbicides in operational prescribed forest fires.

INTRODUCTION

The application of herbicides to forest lands followed weeks later by a prescribed fire is a widely used form of site preparation prior to forest regeneration. In this process, the vegetation at a selected site is often burned 45 to 180 days after herbicide treatment. This forest management practice known as "brown and burn" has raised forest worker and public concerns about possible exposure to herbicide residues in the smoke from the fire.

Modeling assessments have shown that the risk to forest workers is insignificant, even if the fire occurs immediately after herbicide application (as might occur in a wildfire).¹

Until recently, the only field measurements of smoke from herbicide treated sites were made with single point samplers in limited unpublished pilot studies in the South and West. The results from these studies supported the model findings of no significant residues; however, no direct correlation could be made to worker exposure since actual breathing zone concentrations of residues in smoke were not measured under field conditions. To provide that data and to validate the model, we designed monitors to measure the concentrations of herbicides and particulate matter in smoke from prescribed forest fires and measured these concentrations in the breathing zones of workers on 14 operational prescribed fires in Georgia.

METHODS AND RESULTS

SMOKE MONITORS. Two smoke-herbicide monitoring systems were developed for use in this study. One system consisted of a personal monitor worn by forest workers as they carried out their normal duties on the fires. This would represent a realistic-operational scenario for exposure assessment purposes. The second system was a portable area monitor which could be deployed by research personnel and maintained in areas of high smoke concentration. This would represent a worst-case operational scenario. Both systems were designed to simultaneously trap breathing zone concentrations of particulate matter and airborne herbicide residues that might be present in the smoke.

Sampling strategy focused on recovery of parent herbicide compounds which could volatilize in the heat of the prescribed fire. No attempt was made to monitor or analyze for herbicide thermal decomposition products. Under the operational and highly diluted field conditions, the decomposition products would not be detectable or distinguishable from the myriad of similar decomposition products which originate from the burning of the dominant forest biomass fuels (leaves, needles, twigs, etc.).

The sampling cartridge for both systems consisted of a 25 mm diameter three-piece styrene acrylonitrile holder or cassette (Nucleopore # 30015). This cassette is normally used for asbestos sampling, and the 50 mm center section or extension cowl is designed to prevent filter damage during open-face sampling. In our application, the cowl was used to snugly hold a plug of polyurethane foam behind a glass

fiber filter. Thus each cassette was loaded with a 25 mm binder-free glass fiber filter (GFF) (Nucleopore Grade AA # 201618) in line with a 27 mm dia. x 35 mm long cylinder of polyurethane (PUF) foam (Analabs # RCS-083). The GFF and PUF were supported by 25 mm porous plastic support pads (Nucleopore # 220600) to prevent movement in the cassette (Fig. 1). The cassette is held together by a compression fit of the three plastic components. Insurance against leaks can be achieved by placing plastic shrink seals or electrical tape around the two cassette joints.

To monitor the respirable range of smoke particles, the inlet to each personal monitor cassette was fitted with a 10 mm Dorr-Oliver nylon cyclone separator (MSA #456228) (Fig. 2). To make a secure connection between the cyclone and the tapered cassette inlet, the plastic tip of the cyclone vortex finder was replaced with a brass adapter (SKC #225-13-3). Support for this connection was provided by a heavy duty rubber band as shown in Fig. 2. The cyclone is normally operated at 1.7 L/min in order to achieve a 50 percent collection efficiency for 3.5 μ m particles (aerodynamic diameter) in accordance with the American Conference of Governmental Industrial Hygienists criteria for respirable particles. We elected to operate the sampler at 4.0 L/min to improve our detection limit for both particulate matter (via gravimetric methods) and herbicide residues (via chromatographic methods). At 4.0 L/min, the cyclone 50% collection efficiency is lowered to 2.3 μ m according to the findings of Blachman & Lippmann.² To quantify the differences in smoke particle collection efficiency for the two flow rates, a series of small open burn experiments were conducted in a 85 m³ greenhouse. Pine needle and leaf litter were burned to generate smoke. Three pairs of personal monitors w/cyclones were used to monitor the smoke on three separate burns. The 1.7 L/min samplers collected 12 percent more particles than the 4.0 L/min samplers (n=9, coefficient of variation 5.6 percent). This is consistent with the particle collection efficiencies for the two flow rates mentioned earlier.

Several investigators have reported the advantages and collection efficiency of GFF for smoke particulate matter and PUF for pesticide, especially when sampled at relatively high flow rates. When GFF and PUF are combined in a single disposable cassette, they provide a means to simultaneously sample smoke particulate matter and herbicide residues. In our prior work,^{3,4} the GFF proved to be the primary collector for both particulate matter and herbicide residues and the PUF simply provided a back-up for possible herbicide breakthrough, especially if the sampler was exposed to elevated temperatures from the combustion process. To meet the objectives of this study, no pre-treatment or clean-up of PUF's or GFF's was necessary.

Commercial samplers are available which employ the GFF/PUF concept; however, they are too bulky for personal monitoring and for use in a remote field environment. A small portable lightweight system was needed for this study. The Nucleopore sampler was selected over other commercially available monitors because of the fortuitous compression fit of the 27 mm PUF into the 25 mm center section of the 3-piece monitor. In many earlier studies, PUF specifications would normally require tedious custom cutting and fitting of PUF cylinders out of a larger sheet of foam. In this case, all materials were commercially

available at a low cost and usable without further treatment or modification. Total cost of each loaded cassette (without the cyclone) was \$1.58 which permitted a one-time use and thereby minimized logistical problems associated with sampler preparation, storage, transportation, and recycling. Cross contamination problems were also eliminated. The cassette just described was adapted into a personal monitoring system and an area monitoring system.

a. Personal Monitor: The components of the personal monitoring system consisted of a small 1 kg battery operated pump (SKC Model 224) and carrying case. The pump is equipped with a timer, flow disrupt indicator, and internal flow controller to maintain constant flow conditions. The cassette is connected to the pump by flexible tubing which allows the cassette to be clipped near the workers breathing zone while the pump is worn comfortably around the waist, allowing the workers to carry out their normal duties (Fig. 3).

Our desired lower detection level for airborne smoke particulate matter was 150 ug/m^3 , roughly twice the ambient particulate matter background. For herbicide residues, our target airborne detection level was 1 ug/m^3 . This level is well below the concentration range predicted by the modelling method cited in the introduction. It is also a level which is several thousand times below the Threshold Limit Values (TLV) and Permissible Exposure Limits (PEL) for the herbicides 2,4-D (2,4-dichlorophenoxy acetic acid) and picloram. Not all herbicides have published TLV's or PEL's; however, the TLV values for 2,4-D and picloram provide useful benchmarks for occupational risk assessment for the herbicides used in this study. Even when compared to herbicides which do have a high inhalation risk, the 1 ug/m^3 detection level is still conservative. For example, it is 100 times below the TLV for paraquat which has the lowest TLV of all herbicides.

Our personal monitoring strategy anticipated that breathing zone smoke concentrations could vary by a factor of ten depending on weather, fire conditions, and worker assignment. In addition, smoke exposure times in any given day would vary depending on the size and number of tracts to be burned. In the case of a 4 hour exposure; a monitor with flow rate of 4 L/min, coupled with a gravimetric analysis of the filter to the nearest $0.01 \pm 0.005 \text{ mg}$ would yield a smoke particulate matter detection level of $104 \pm 5 \text{ ug/m}^3$. Those same conditions when coupled with a herbicide chromatographic detection level in the lab of 1 ug/sample would yield a herbicide detection level of 1 ug/m^3 .

b. Area Monitor: To simulate worst case operational conditions on each site without compromising normal worker behavior and operations, an area monitoring system was also deployed on each fire by research personnel. The need for rapid deployment and repositioning during the fire called for a relatively lightweight, battery operated system which could be carried by one person in relatively uneven forest terrain. In addition, a system with higher flow rates than available on personnel monitors was desirable to enhance our detection capability. The system used on this study consisted of a small, 10.5 kg air sampler (Gilian Model Aircon 520 DCT) powered by a small, 9.5 kg 12 V deep cycle marine battery. The aircon 520 consists of a integral flow controller mounted

on a 12 V dc pump and shock mounted into a compact enclosure. It also includes a built-in rotameter, a flow control valve to adjust the flowrate from 2 to 22 L/min, a suction/pressure gauge to indicate actual load, an elapsed timer, and a built-in telescopic sampling mast to permit "breathing zone" sampling at the 5 ft level. The sampling cassette used on the area monitor was identical to the one used on the personnel monitor minus the cyclone particle size separator. Operating the area monitor without the cyclone permitted collection of both respirable smoke particles generated by the combustion process as well as some of the mechanically generated and inhalable soil/dust particles. Thus the area sampler provided a means of collecting herbicide residues which could volatilize and residues made airborne by mechanical disturbances of the soil. Operation of the area monitor at 20 L/min (5 times the rate of the personal monitor) would achieve the desired herbicide detection level of 1 ug/m^3 in only 50 min of sampling.

Preliminary tests with the small marine battery demonstrated at least one hour operating time at 20 L/min even under high smoke concentrations. While larger batteries are available, the small battery permitted one person to easily transport the entire system with the weight balanced between both hands (Fig. 4). Backup batteries and preloaded cassette samplers were available on site to monitor for longer periods or to obtain time-sequenced samples as dictated by fire and smoke conditions on the site.

c. Herbicide Recovery Experiments: The trapping efficiency and laboratory recovery of pesticides from GFF's and PUF's had been shown to be effective in prior laboratory combustion studies.^{3,4} However, a retention efficiency experiment under the highest sampler flow conditions (20 L/min) was deemed necessary and performed for each of the herbicides to be studied. Recoveries are shown in Table 1. Results are given in conjunction with freezer storage periods which approximate the storage period for test fire samples. All of the residues recovered from hexazinone, triclopyr and picloram were found in the glass fiber filters. A small percentage of the overall recovery (11%) of imazapyr was found in two of the four PUF samples analyzed. These filter/PUF recovery ratios are consistent with results from our prior studies with pesticides and with the results of Roberts and Ruby⁵ who found less than 0.1% of semivolatile pesticides collected from dust particles to pass through the filter to the PUF. These findings question the need to include the PUF component as a part of the collection media when dealing with low volatility chemicals such as the herbicides used in this study. However, to be on the safe side, we included the PUF component in this study as a backup collector, even though it required a separate analysis and therefore increased analytical costs.

SMOKE MONITORING PROCEDURES. The forest workers conducting the burning operation were outfitted with personal monitors. The pumps were activated just prior to ignition and deactivated when the crew reassembled to leave the fire site. If there was more than one fire in a day, the process would be repeated with fresh cassettes for each fire. Workers were encouraged to perform their duties using their normal operational procedures.

At each fire site, three area monitors were deployed to separate locations and repositioned as necessary by research personnel to areas with high breathing zone smoke concentrations. All of the sites had numerous access areas (firelines, paths, roads) in and around the burn area which allowed moving the area samplers without compromising personal safety. After initial placement and activation of the area monitors, the research personnel moved back to a relatively smoke free area and periodically visited the area sampler site to check flow rates, move the sampler and/or change cassettes as necessary. The time of operation for the area sampler varied depending on smoke conditions and filter loading. At the end of each sampling period and/or each fire, pump operating time was recorded and flow rates were visually verified. The labeled cassettes were capped and stored in an ice chest for return to the laboratory for gravimetric and chromatographic analysis.

The monitors were used successfully on 14 operational prescribed fires in Georgia. Tract size ranged from 6 to 380 acres. No herbicide residues were detected in either the personal or area monitors (detection range to 0.1 to 4.0 $\mu\text{g}/\text{m}^3$). Worker respirable (2.3 μm particle cutpoint) particulate matter concentrations ranged from 248 and 3,723 $\mu\text{g}/\text{m}^3$ with a mean of 1,429 $\mu\text{g}/\text{m}^3$. Exposure times ranged from 1.2 to 6.3 hours with a mean of 2.8 hours. Area monitor particulate concentrations (ranged from 2,000 and 45,000 $\mu\text{g}/\text{m}^3$ with a mean of 8,219 $\mu\text{g}/\text{m}^3$).

ACKNOWLEDGEMENT

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Table 1. Percent herbicide recovered from spiked sampling cassettes.^a

Herbicide	Without aspiration	With aspiration ^b	freezer storage period at -10°C weeks
	-----percent-----		
Imazypyr	73 ± 20 ^c	89 ± 14	12
Hexazinone	95 ± 8	92 ± 8	6
Triclopyr	125 ± 7	88 ± 2	11
Picloram	85 ± 7	71 ± 14	14

^a20 ug spike all samples (n=4).

^b20 L/min for 1 hr at 78°F and 55% RH.

^cMean (± SD).

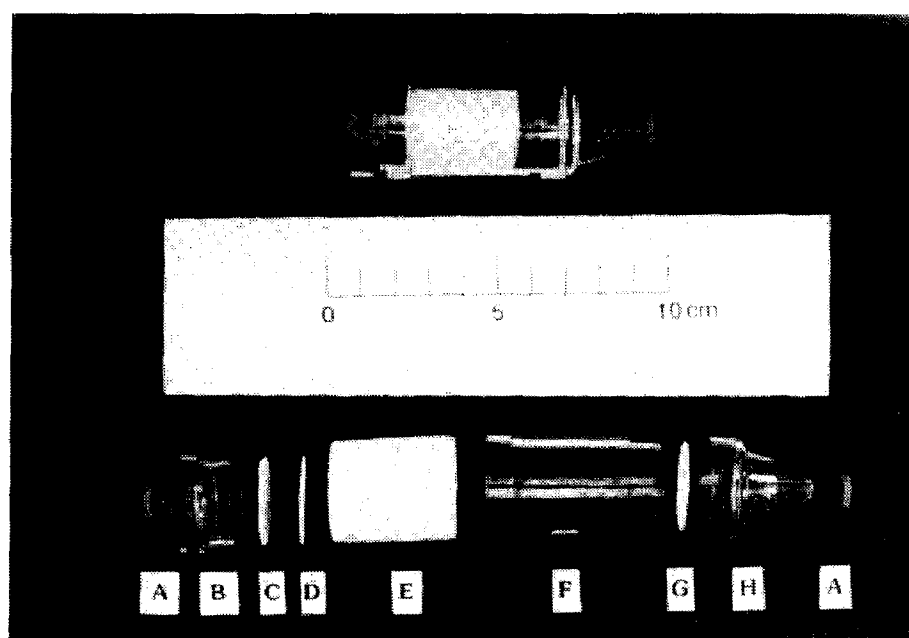


Figure 1. Smoke sampling cassette (upper), exploded view (lower). A, end plugs; B, inlet; C, glass fiber filter; D and G, porous plastic support pads; E, polyurethane foam; F, 50 mm extension cowl; H, base.

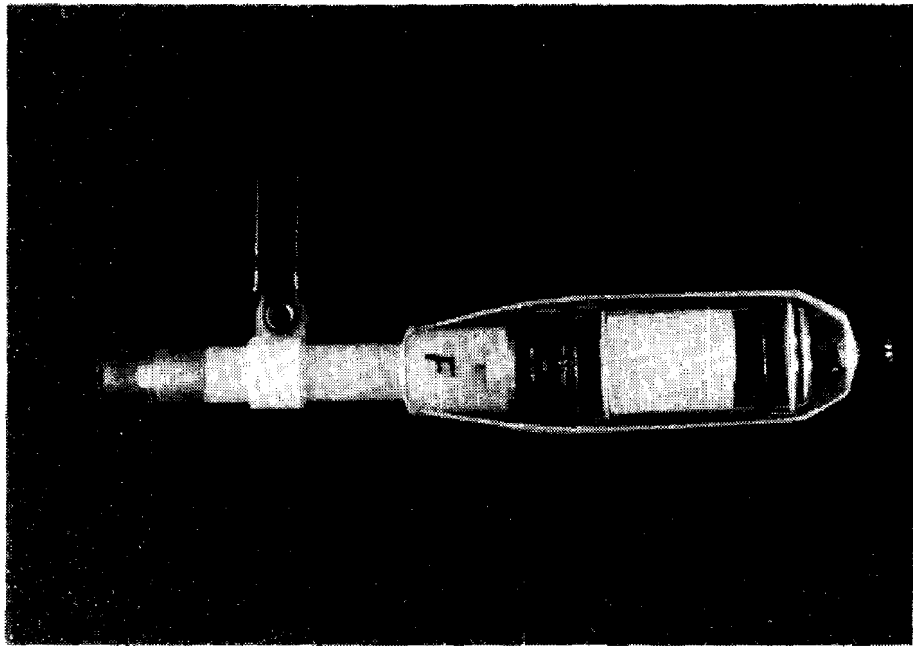


Figure 2. Smoke sampling cassette with 10 mm nylon cyclone connected to inlet for sampling respirable particles.

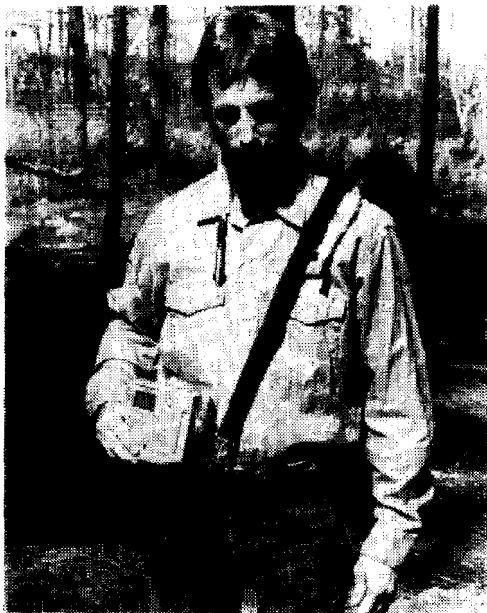


Figure 3. Personal monitoring system for prescribed fire smoke. Sampling cassette with cyclone is worn at workers breathing zone.



Figure 4. Area monitoring system for prescribed fire smoke. Sampling cassette is located on telescopic mast at the 5 ft breathing zone level.

DEVELOPMENT OF A TEST ATMOSPHERE GENERATION FACILITY FOR PARTICLE BOUND ORGANIC COMPOUNDS

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ABSTRACT

A test atmosphere generation chamber has been developed to generate particles containing PAH and volatile organic compounds. Initially, work emphasized the characterization of the apparatus and development of particle generation methods using generators based on dust feeding or vibrating orifice aerosol generation techniques. Some of this work has been reported elsewhere. In current work, further development has been performed on generation methods and the apparatus has been used for its intended purpose (i.e., to examine sampling methods for these compounds). Specifically, tests on a PAH vapour condensation method were performed to develop a suitable protocol for generation of artificial aerosols containing PAH. Also, different types of sampling trains suitable for indoor air quality assessment and determination of airborne compounds in occupational situations were examined. Included in the testing were investigations of aerosol generation of particle bound organics and of performance of different sampling trains for airborne PAH. Some features of the apparatus and preliminary data are presented demonstrating the utility of the apparatus and outlining some comparative results.

INTRODUCTION

Measurement of ambient air in residential and occupational environments for volatile, semi-volatile compounds (light PAH) and particle bound organics (heavy PAH), required the development of suitable measurement methods. A prerequisite for this activity is development of a laboratory test atmosphere generation system. Hence, the creation of such a facility was established as a primary objective. The technical specifications of the

various components were established from the basic principles of test atmosphere generation as set out by G.O. Nelson (1971) and on the basis of a literature review (Guerin and Fellin, 1985). A preliminary design of a test atmosphere generation system (TAGS) was prepared that included various generation options for particles and vapours. In subsequent phases of the program the apparatus was assembled and subjected to preliminary tests to evaluate its performance with a tracer gas, CO₂. One of the particle generation options identified, a dust generator instrument, was also adapted to the inlet (Particle Source - Figure 1) and utilized to conduct preliminary characterization of the apparatus. These tests were reported in Fellin et al., 1987 and Fellin et al., 1988. Further testing of the apparatus using a vibrating orifice monodisperse aerosol generation method (VOAG) as outlined by Berglund and Liu (1973) was performed. Coupling the VOAG and a PAH generator based on diffusion tubes was attempted to generate particle-bound organics. Preliminary results of these tests were reported in Fellin et al., 1988a. This paper reports on further testing and optimization work which has been performed since these initial studies were completed and evaluates the progress made toward establishing a test atmosphere generation facility suitable for particle-bound and volatile organic compounds.

EXPERIMENTAL

The apparatus employed for testing is shown in Figure 1. The major components were the particle generation instruments (Figure 1A and 1B). These were the Wright Dust Generator (WDF) Instrument (Model II, BGI. Inc.) and a custom designed apparatus that incorporated a vibrating orifice aerosol generation (VOAG) apparatus (Berglund - Liu type, Model 3050, Thermo Systems Inc. (TSI)). Dust generation employed NIST standard reference material no. 1649 that was certified for 5 PAH. Data on 14 other PAH compounds was provided in NIST documentation. The diluent air source, chamber and exhaust system have been described previously (Fellin et al., 1988). Particle size distributions and concentrations were measured using a piezoelectric quartz micro balance 10 stage impactor (QCM) (Model PC2 California Measurements Inc.), an Andersen 8 stage impactor (Model 0704, Andersen Inc.) and 37 mm polypropylene integrative filter units incorporating glass fibre filters (Type TX 40H120-WW, Pallflex Products). Vapour concentrations of PAH were monitored using Orbo 43 sorbent (Supelco Inc.). Cyclones for some of the sampling trains were provided by Levitt Safety Ltd. (cat. no. IV3799) and had a particle size cutoff of 50% at 2.5 µm when operated at a flow rate of 1.7 L/min. Gravimetric analyses were performed on a Sartorius (Model 2004 MP, Sartorius Balance) 5 place analytical balance. For vibrating orifice aerosol characterization tests, filters were extracted with water and extracts were analyzed on an ion exchange chromatograph (Model 10, Dionex Corp.). PAH were extracted from filters and sorbents with methylene chloride and extracts were analyzed by gas chromatography/mass spectrometry using an HP 5890 GC fitted with a 30 m DB-5 capillary column. The GC column was directly inserted into the source of an Ion Trap Detector (Model 800, Finnegan Instruments). For some tests excess PAH vapours were removed by using a hollow tube denuder placed in the transfer tubing between the condensation chamber and the aerosol dilutor (Figure 1B). Charcoal impregnated GoreTex (W.L. Gore and Associates) inserted inside the 1 inch I.D. x 12 in. long transfer line served as the sorbent.

RESULTS

Previous tests had investigated the performance of the WDF in the TAGS and established optimal operational settings. The particle size distribution achieved with the WDF (Figure 2) demonstrates significant bias toward particle sizes greater than 2.5 microns. Since the dust generated was based on NIST standard reference material no. 1649 Urban Particulate Dust which had nominal particle sizes or mass median diameters (mmd) below 2.5 microns when it was collected, the results suggest aggregation of particles during

generation steps. Homogeneity of particle distribution was examined by sampling at 9 points inside the exposure zone of the chamber (Figure 1C) over 6 to 8 h with integrative filter samplers. The results are featured in Table 1 for particle mass collected and Figure 2 for particle size distribution. Similar results were evident when data were stratified vertically (Y results) or horizontally (X results). Overall reproducibility using gravimetric analysis, as defined by the precision estimates, approached $\pm 15\%$. It is important to recognize, however, that mass collected on each filter element was relatively low (0.01 g or less) because of the low flow rates employed (1-2 L/min) during the tests. Hence significant imprecision in the gravimetric measurement step is introduced. The results suggest the particle concentrations in different locations of the chamber were statistically indistinguishable and sampling conducted in the exposure zone would not be biased by sampler location.

The vibrating orifice aerosol generator was employed to assess several operational aspects of the TAGS performance. The production of sub-micron sized aerosols was established as a primary objective. Several salt (NaCl) solutions of different concentrations were tested as feed solutions for the VOAG to achieve this, but no success was achieved until a TSI representative suggested that using impurities in the isopropanol solutions without salt addition could lead to consistent production of sub-micron sized monodispersed aerosols. Monodisperse aerosols were produced in the TAGS with a mass median diameter of 0.8 microns by using the unmodified isopropanol, as determined with the QCM microbalance. Comparison of salt impregnated solution and isopropanol solutions provided in Figure 3 describes the size distributions achieved. When PAH was added to the particles by the vapour condensation method shown in Figure 1B, a coating efficiency for phenanthrene of 2-3% was found. The net impact of this was to allow much of the PAH to enter the TAGS exposure zone in the vapour form. A diffusion denuder was created to remove the vapour PAH by insertion of charcoal impregnated GoreTex in the transfer tubing positioned ahead of the TAGS mixer (Figure 1). GoreTex was found to be a strong sorbent for PAH in previous work. Calculations performed according to Gormley and Kennedy (1949) to estimate denuder performance and Fuller et al. (1973) to evaluate PAH diffusivity suggested a theoretical removal efficiency using a hollow tube configuration for the denuder of 0.23 under one set of conditions. Tests indicated that the maximum removal achieved was 0.20. This agreement is quite reasonable considering the denuder dimensions employed and the uncertainties inherent in the estimation of the diffusivity of phenanthrene. The relative success of these tests suggests it may be worthwhile to redesign the inlet to incorporate an annular denuder to improve the removal efficiency for the vapour component of the PAH to 95% or better.

The VOAG/PAH condensation technique was also employed to conduct preliminary tests of sampling trains consisting of sorbent, filter-sorbent and cyclone-filter-sorbent configurations. In these tests it was found that collection of phenanthrene by use of a sorbent tube gave the highest results ($280 \pm 8\%$ ng/sample) compared with $220 \pm 8\%$ ng/sample for filter/sorbent tube combinations and $200 \pm 6\%$ ng/sample when a cyclone was added. All results quoted were normalized to the same total volume of air sampled and were adjusted for recovery efficiency. The results indicated differences among the different sampling methods of up to 40% in the data for one PAH. These differences are difficult to explain based on the random sampling positions employed for sampling and the careful attention paid to monitoring and controlling the volume of air collected.

In conclusion, the TAGS has been established as a test facility. Its operation is suitable when using dusts generated by means of WDF methods. However, this method produces significant particle concentrations in the size ranges greater than 2.5 microns. Aerosol generation via the VOAG has achieved particle sizes in the sub-micron range and PAH precoated particles can be generated. However, the condensation process is relatively

inefficient with phenanthrene, the PAH used for testing. Removal of excess vapour form of PAH has also been demonstrated using a diffusion denuder. Results suggest that efficient use of the denuder requires redesign of the inlet to achieve removal efficiencies of 95% or better since the current inlet can only achieve removal of 20%.

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TABLE 1

Determination of Chamber Bias by Monitoring at Different Sampling Points with Integrative Filters

- Longitudinal Precision (n = 17)

X_1	\pm	14%
X_2	\pm	6%
X_3	\pm	14%

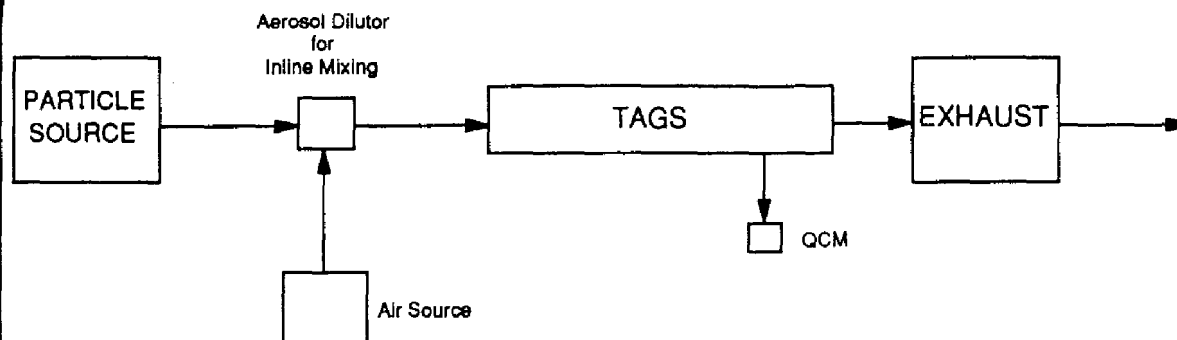
- Vertical Precision (n = 17)

Y_1	\pm	11%
Y_2	\pm	7%
Y_3	\pm	7%

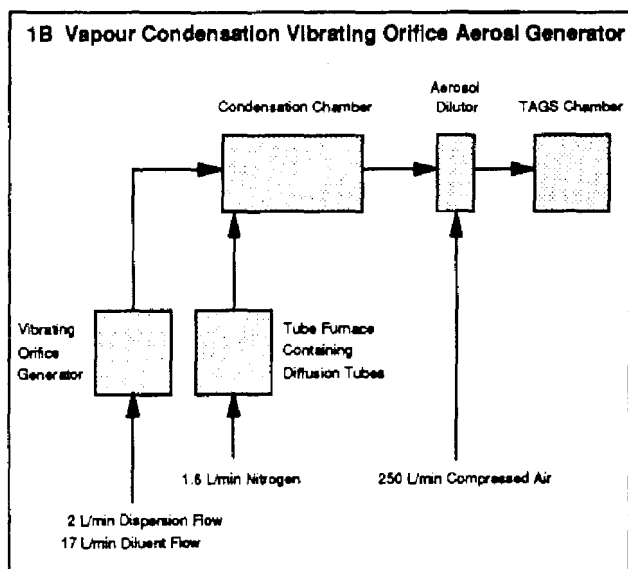
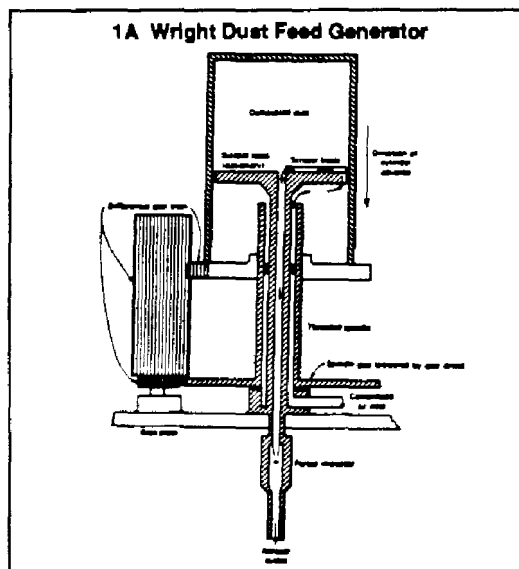
- Overall Precision $\pm 15\%$

No consistent vertical or horizontal bias was noted.

FIGURE 1
Test Apparatus



Particle Sources



1C Tags Chamber

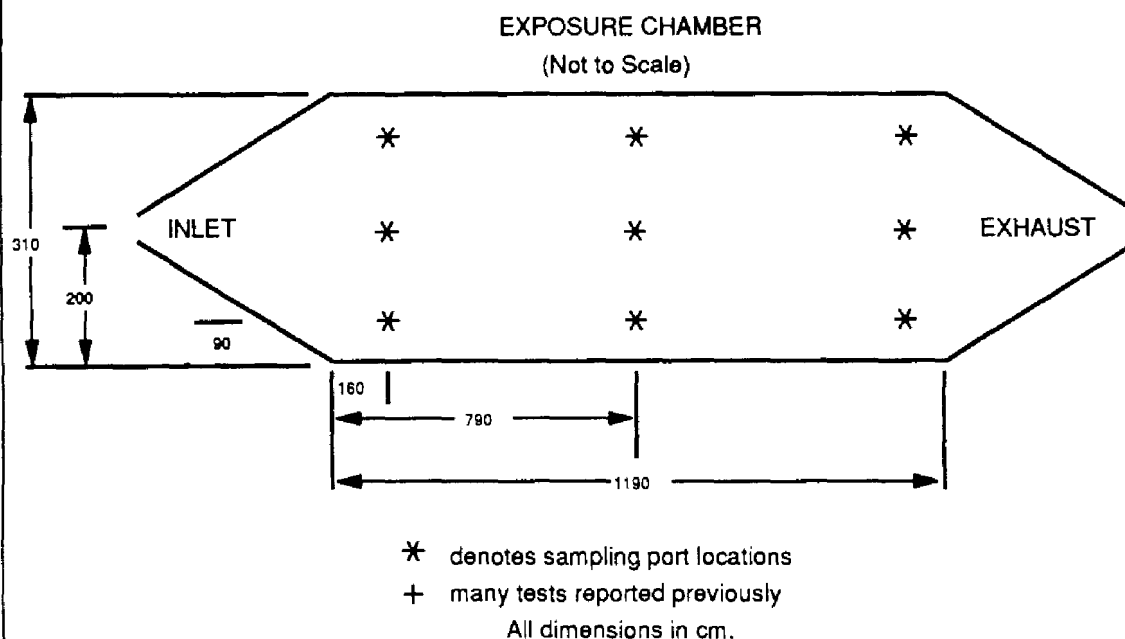


FIGURE 2

Evaluation of WDF as Particle Feeder for TAGS
Typical Size Distribution Results
(NIST 1649 Dust)

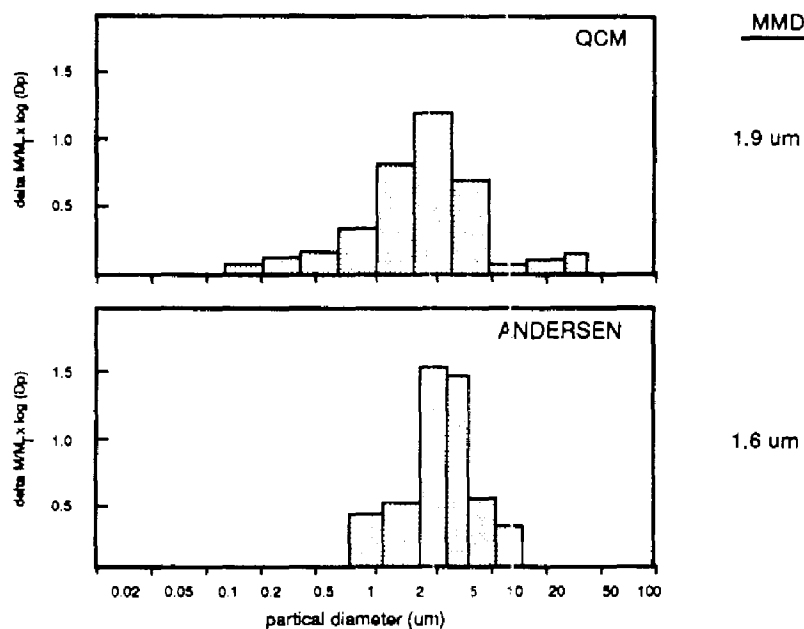
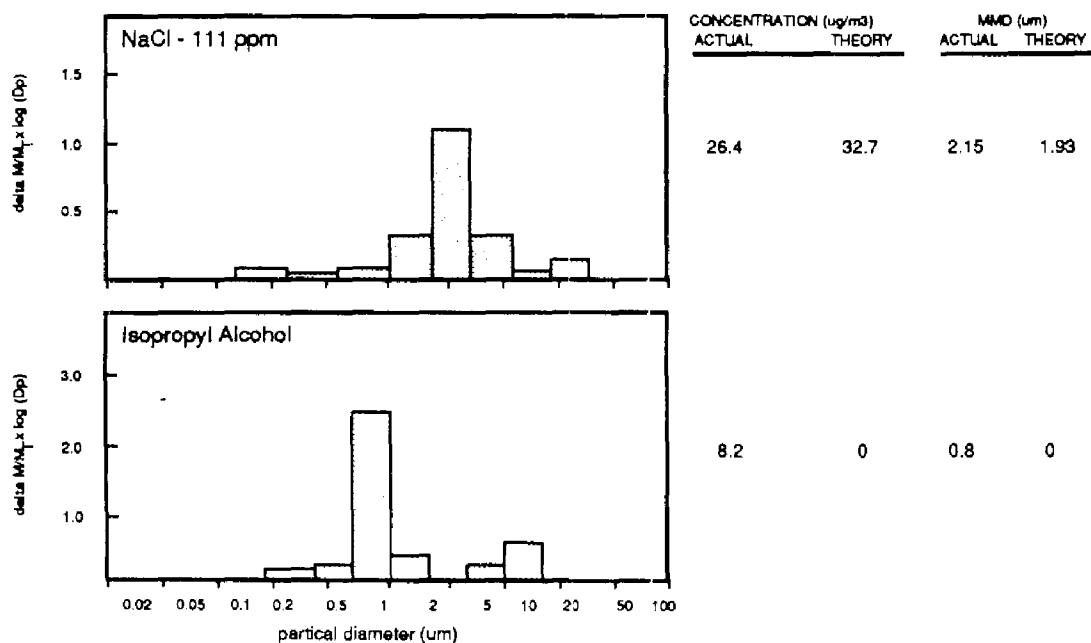


FIGURE 3

Typical Particle Size Distribution



Spectroscopic Identification of Organic Compounds by Library Searching: Methods, Potentialities, Limitations.

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1. Overview.

Library search for the structure elucidation and identification of organic compounds seems to be a very simple and straight forward technique. First we record the spectra of the sample at hand. The spectra of the sample are then compared to all reference spectra in a reference library. If there is a sufficiently close match between the unknown sample's spectra with one of the reference spectra, the chemical structure of the respective reference compound is believed to be similar to the sample's chemical structure. This process is schematically represented in fig. 1. To gain insight into the potentials and limitations of this seemingly simple process a somewhat more detailed system analysis is helpful.

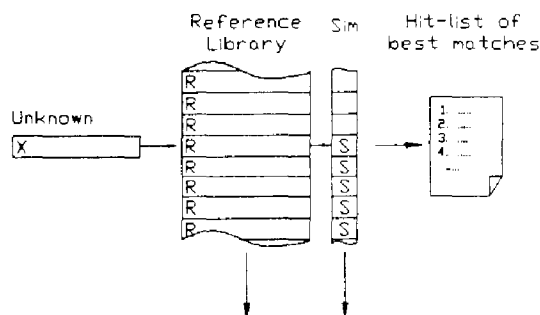


Fig. 1. Library Search. The spectrum of the unknown X is compared to all spectra of the reference compounds R in the reference library, and the degree of similarity S is evaluated. The reference compounds most similar to the unknown are then put out.

2. The Basic Model.

The most important thing to realize when working with library search systems is that when we compare spectra we really mean chemical structures. We tacitly assume that similar spectra imply similar chemical structures. If in a library search system this hypothesis is not adequately met, the respective system will be useless for practical applications. This is a required but not sufficient condition for a library search system to be useful. Thus, in order to understand library search, one has to understand the comparison process. The central hypothesis of library search is "If the spectra are similar then the chemical structures are similar." This statement is often referred to as the library search hypothesis. Whether it is true or not obviously depends on what is meant by "similar". We consider two objects to be similar if they are identical in many aspects believed to be relevant in the given context. Similarity thus requires that the objects to be compared are characterized by many different features which can be either identical or different. A simple measure of the similarity between two objects is the number of corresponding features in which they are identical. A chemical compound and its spectra are thus characterized by a set of structural descriptors and by a set of spectral descriptors. One may now set up two independent multidimensional spaces for structures and spectra respectively, where one descriptor is assigned to each coordinate axis from the respective set. Every conceivable chemical compound characterized by its spectra can now be mapped into a point in each of these multidimensional spaces, using the values of the respective descriptors as coordinate values. The two spaces are referred to as the structure space and the spectra

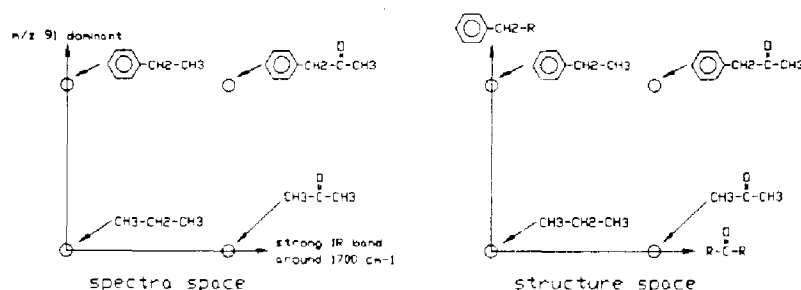


Fig. 2. Spectra space and structure space for 4 simple compounds. Spectra and structures are characterized by selected features. The feature states are then used as coordinate values in the respective coordinate system.

space respectively. A very simple example is given in fig. 2.

Comparing the spectra of two compounds amounts to measuring the distance between their respective points in the spectra space. The more close they are, the more similar are the two spectra. If the two points coincide, the spectra are considered as identical. The library search hypothesis now requires that

points close together in the spectra space are also close together in the structure space, i.e. the two spaces should have the same (mathematical) structure (see fig. 3).

The spectral features defining the spectra space and the distance measure to be used in this space are an integral part of any library search system. The goal in selecting the descriptors and in defining the distance measure is to model in the spectra space the (mathematical) structure of the structure space as closely as possible. Similarity in the structure space, however, is not defined and depends on the problem to be solved and on the user and his preferences. Thus, no library search system can work well for all applications.

3. Feature Selection.

The spectral features selected to describe the spectra and to span the spectra space determine how well the spectra space will conform to the structure space. One wants the spectral features to be sensitive to differences in the chemical structure, but insensitive to technical and instrumental conditions.

In some applications one may assume that the unknown samples are represented in the reference library. This is often the case in environmental analysis and in government laboratories, where the question is whether the sample is a compound specified in a (limited) list. Here, the degree of structural sensitivity of the features selected is of no great concern. The system is expected to identify all compounds in the list. If a sample is another compound, the answer "not identical to a reference compound" is interpreted as "not on the list" and is accepted as such. Applications of this type are referred to as identity search.

However, if the question is "What is it?", then feature selection becomes much more difficult. If the sample is not identical to one of the reference compounds, the user expects to be presented with a set of model compounds similar to the unknown and uses the similarity measure (distance in the spectra space) as an estimate of structural similarity (distance in the structure space). To get reasonable correlation between the two similarity measures the spectral features have to be selected with care. This type of application is referred to as similarity search.

4. Size and Contents of the Library.

All library search systems have one fundamental limitation. The set of answers they can provide the user with is limited by the contents of the reference library. If, for a given unknown, no suitable reference compound is part of the library, no useful answer can ever result, independent of all other factors. Thus, size and contents of the reference library are of fundamental importance for the performance of the system.

For an identity search system it is obvious that the library has to include all compounds to be identified. The larger the library, the more compounds we can successfully deal with. However, the other aspects of the performance are not increased by additional compounds. On the contrary, search time and thus costs will increase with the size of the library.

For similarity search systems, suitable reference compounds for all conceivable unknowns are required. This seems to call for a comprehensive library containing the spectra of all known chemical compounds or at least as many as one can get hold off. However, a moment's reflection shows that this is not the optimal solution. For each compound type one needs just one or maybe a few references. Large sets of closely related reference compounds will, in a true similarity search system, not increase the performance. On the contrary, retrieving an excessive number of closely similar references for a given sample will just increase the output volume without providing additional information. It is only the first reference compound in a group of related compounds which matters. The other references, being very similar to the first one, just repeat the same message over and over again.

What one really needs can be clearly stated within the space model (see fig. 4): The spectra space has to be filled sparsely but evenly with reference compounds, to provide some close neighbors in every section

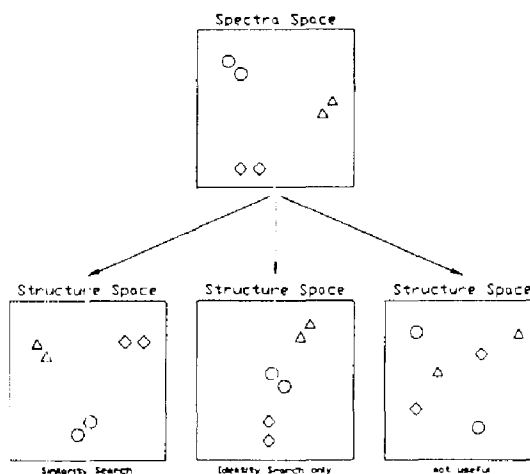


Fig. 3. Relations between spectra space and structure space. Similarity between spectra and between structures is related to distance between the respective points. If both spaces have globally the same (mathematical) structure, distances (and thus similarities) may freely be transferred between the two spaces (left). If the relation holds only locally, only high similarities approaching identity are meaningful (centre). If the two spaces have different structures, the respective system is not useful.

of the space. The correspondence between spectra space and structure space insures that in this case the structure space will also be adequately populated. The population density should reflect the relevance of the respective space sector to the user. In his fields of interest the average number of references may be higher than elsewhere, in order to give a higher resolution. Thus, an optimal library will consist of two parts. A general part, which provides a few prototype compounds for every compound class, and one or more special parts, documenting the user's field(s) of interest with enhanced resolution.

To ensure wide coverage of all fields and branches of chemistry, the general part of a reference library will generally have to be bought from an outside source. The special parts, however, have to be assembled by the user himself. All the spectra recorded in his laboratory are important in this context, even if the respective compounds have no other relevance. The fact that the respective sample has been submitted for analysis is a prove that it is relevant to the analyst. Thus, all spectra recorded in the user's lab are candidates for inclusion in the reference library. However, to limit the size of the reference library only the spectra of compounds from classes not yet adequately represented in the library should be added.

5. Evaluation of the Performance.

The performance of a library search system includes many different aspects. First of all, we expect a powerful library search system to be able to retrieve from the reference library compounds identical to the samples, if such compounds exist in the library. If no compound identical to a given sample exists in the library, the system should provide the user with reference compounds structurally similar to the unknown. It should be able to do so regardless of the technical parameters used when recording the respective spectra. To each reference retrieved a reasonable measure of similarity to the unknown should be put out. These similarity values have to inform the user whether a given reference compound can be assumed to be structurally identical to the sample with high probability or whether it is similar only. In the latter case the similarity measure should give a reasonable estimate of the structural similarity. Furthermore, we expect the library search system to be fast, to be easy to use and to present the results in easily interpretable form. Finally, there have to be program modules which allow for easy maintenance of the system library. In particular it should be easy to add, delete and edit entries. Evaluating a library search system amounts to assigning values (measured at least on an ordinal scale) to all these aspects of performance. In the present lecture no attempt is made to discuss the aspects which depend to a large extent of the user's personal taste, i.e. the presentation of the results and the quality of the user interface. The only topic to be discussed is how to estimate the quality of the results from a chemical point of view.

6. General considerations.

The most important qualifier for a library search system is how well it maps spectral similarity into structural similarity. The fundamental problem here is that presently no generally accepted similarity concepts for chemical structures exist. The chemist's notion of structural similarity is strongly coined by traditional views (functional groups, skeletons, compound classes) and by the problem he currently studies. Furthermore, different spectroscopic techniques focus on different structural entities and are thus inherently biased towards certain aspects of structural similarity. Thus, no generally applicable procedure can be given.

A second problem arises from the fact that the composition of the reference library is of paramount importance. The set of possible answers is limited to the chemical structures represented in the library. A system to be tested can produce a useful answer only if its library contains at least one suitable reference compound for the test sample. Thus an unlucky choice of test samples can shift an otherwise excellent system the bottom of the list.

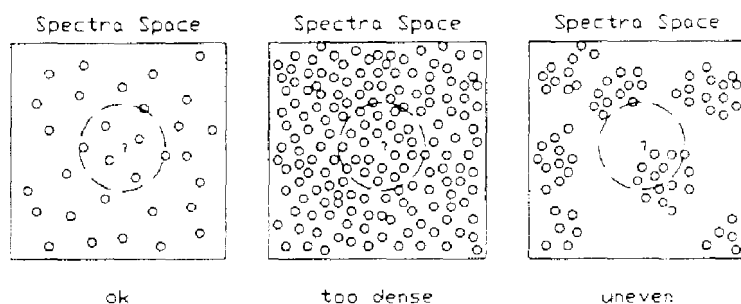


Fig. 4. Point density and distribution in spectra space. The points corresponding to the reference compounds most similar to the unknown lie within a circle centered on the unknown, its radius being given by the smallest useful similarity. If the density of reference points is too high, the number of close matches becomes unmanageable (centre). An uneven distribution gives a biased result.

7. Test procedure.

Both these problems can be solved by using a standardized test library to be used by all systems to be compared. The user should carefully select a set of about ten to twenty test compounds and record their spectra under strictly routine conditions. It is important that user selects these compounds to be truly representative for the compound classes he predominantly deals with in his practical work. This ensures that the test is performed in the regions of the spectra and structure space most important to the user. The test compounds are grouped in subgroups (preferably triplets) containing at least one pair of (structurally) highly similar compounds and one pair with moderate structural similarity, the degree of structural similarity being subjectively judged by the user in the context of his daily routine work. With this choice the user implicitly defines his concepts of structural similarity. Between the subgroups, however, the structural similarity should be low. One or a few compounds should be duplicated, i.e. their spectra should be recorded twice under different conditions (different matrix and/or different instrument settings).

The test spectra are then assembled into a mini reference library to be used by all systems to be tested. The same spectra will also be used as test samples. Each sample compound is submitted to the system as an unknown, and for all references the similarity computed by the system is noted. The data are best organized into a similarity matrix. Each unknown is assigned to a row, the columns are assigned to the references, and the members of subgroups of mutually similar compounds are kept together.

This procedure makes sure that for each test sample there is at least one structurally identical compound in the library. Furthermore, for each sample there are one or more references which the user considers to be structurally similar. The duplicates will give information on how well the systems under test can handle variations due to technical artifacts.

8. Data Interpretation.

From the similarity matrix a wealth of information regarding the behavior of the system under test may be obtained (cf. fig. 4). The diagonal elements correspond to comparing two identical spectra. Their values will correspond to the highest possible similarity, namely to perfect identity. If this is not the case, the mathematics of the system are wrong, the system behaves irrationally and further tests are unnecessary.

The rows and the columns for the duplicated samples show how well the system can deal with instrumental and technical variations. In the ideal case, the respective rows and columns should be identical (However, a row is not necessarily identical to its corresponding row, the similarity matrix not necessarily being symmetrical). Any differences between corresponding values are due to the fact that the system misinterprets technical variations as being caused by structural differences. In a real system this is unavoidable. The rms difference between corresponding values is a measure for the amount of noise generated by different registration parameters and/or different matrices. Differences in similarity are meaningful only if they are significantly greater than this value.

Off-diagonal elements for duplicates should exhibit similarity values not significantly smaller than the diagonal elements. Failure to do so indicates that the system, being too sensitive for instrument settings and matrix effects, is unable to reliably recognize the identity of compounds.

In the submatrices corresponding to subgroups of mutually similar compounds all off-diagonal elements should be significantly smaller than the values for duplicate compounds, to indicate to the user that sample and reference are not identical. If this condition is not met, then the system has troubles in discriminating between true identity and high similarity. The values should, however, be significantly greater than the values for off-diagonal elements not being in a submatrix for a subgroup, to indicate that the respective compounds are definitely more similar as

	A	A	B	X	X	Y	AB	AX	XY
A	(a)	(b)	(c)	(d)	(d)	(d)	(e)	(h)	(g)
A	(b)	(a)	(c)	(d)	(d)	(d)	(e)	(h)	(g)
B	(c)	(c)	(a)	(d)	(d)	(d)	(f)	(i)	(g)
X	(d)	(d)	(d)	(a)	(b)	(c)	(g)	(h)	(e)
X	(d)	(d)	(d)	(b)	(a)	(c)	(g)	(h)	(e)
Y	(d)	(d)	(d)	(c)	(c)	(a)	(g)	(i)	(f)
AB	(e)	(e)	(f)	(g)	(g)	(g)	(a)		
AX	(h)	(h)	(i)	(h)	(h)	(i)		(a)	
XY	(g)	(g)	(g)	(e)	(e)	(f)			(a)

Fig. 5. Similarity matrix for a simple test setup. Compounds A and B, and X and Y are highly similar, similarity between A or B and X or Y is low. AB, AX, and AY are 1:1 mixtures of the respective pure compounds.

The (a) values give the limiting similarity value for perfect identity. Comparisons between the two A (and X) rows (and columns) measure the noise due to technical artifacts. The tolerance for identity is given by comparing (b) to (a). Discrimination between identity and high similarity is measured by (c) vs. (b), and between high and low similarity by (d) vs. (c). Sensitivity to impurities of high similarity are found in (e) vs. (b) in the case of identity, in (e) and (f) vs. (c) for high, and in (g) vs (d) for low similarity. For impurities of low similarity the respective comparisons are (h) vs. (b), (i) vs (c), and (h),(i) vs (d).

two compounds picked at random. There are two ways to violate this requirement. There can be some elements in the remainder of the matrix which are exceptionally high. As long as there are only a few such entries, this is of no great concern. It is just an indication that the system's inherent similarity concept for structures includes some aspects neither obvious nor relevant to the user. The other case, some elements in the submatrix being too small however, has to be taken seriously. It indicates that the system's similarity measure does not consider certain aspects definitely important to the user. Finally, the sequence of similarity values should reflect the different degrees of structural similarity expected by the user. However, only differences clearly above the noise level are meaningful for ranking.

The information extracted from the similarity matrix as stated above will give a reasonably clear indications as to whether the system under test uses basically the same similarity concepts as the user and whether its sensitivity to structural variations and its insensitivity to instrumental and technical parameters is low enough to give sufficient discrimination between the cases of identity, of high similarity and of no similarity.

One important point has to be kept in mind, however. The above qualifiers are to a large extent subjective. They measure the degree of correspondence between the user's and the system's concepts of structural similarity. The system's similarity concepts are defined implicitly by the designer, mainly by the spectral features selected for comparing spectra. They define the overall mathematical structure of the spectra space and its mapping into the structure space. By selecting groups of (in his opinion) structurally similar test compounds the user defines (again implicitly) the local mathematical structure of the spectra space. Thus, a given system not exhibiting top performance only proves that the system under test does not use structural similarity concepts similar to the user's. This may be due to a poor design of the system or due to the user's expectations being too specialized or irrational. Failure to perform as expected thus disqualifies a system only within the context specified by the test compounds. For other applications the respective system may well be the perfect choice.

Analysis of the similarity matrix can also supply information as to the search strategy implemented in the system. Under the assumption that the test compounds have been well selected, the following procedure reveals the respective information. First, all entries relating to identical spectra (diagonal elements only, not duplicates) are removed from the matrix. The remaining entries are ranked in decreasing order of similarity. Then one prepares a plot of similarity versus rank. This will give a curve which starts at rank 1 with a very high value for similarity and which subsequently drops to the lower similarity values for the later ranking pairs. The general shape of this curve is related to the search strategy employed by the system.

A similarity search system (as opposed to an identity search system) is expected to be able to retrieve reference compounds structurally similar to an unknown sample. Furthermore, the similarity measure should be able to discriminate between different degrees of similarity. Thus, the data set containing user selected pairs of high but variable similarity, the first part of the curve should be a smoothly declining curve, preferably almost linear. The length of the section to be considered is given by the number of off-diagonal elements in submatrices corresponding to the groups of structurally similar compounds. The shape of the remaining curve is of no concern (Nobody cares how useless a useless reference is). In an identity search system one expects positive identification of identical pairs, but places no particular emphasis on the similarity of non-identical pairs. The rank-vs-similarity curve thus starts with a short almost horizontal section, whose length is given by the number of duplicate pairs in the test set. The curve should then drop sharply and level off slowly. Of course, there is a gradual transition between the two pure strategies, resulting in curve shapes somewhere between these extremes. However, a rough estimate of the search strategy is generally possible.

An important part of the search strategy cannot be evaluated from the data in the similarity matrix. All similarity measures employed in library search systems are in some way based on the number of elementary spectral attributes (spectral features) having identical attribute states (the same value) in the two spectra to be compared. This number is set in relation to the total number of attributes considered. If all attributes do have the same state, the system considers the two spectra to be identical. Thus, the degree of similarity is measured as the number of attribute states identical between the two spectra compared, relative to the number of attribute states identical between one of the two spectra compared to itself. Whether the spectrum of the unknown or the spectrum of the reference is used as the base can lead to large differences in the system's behavior. This is most easily explained using a strongly simplified mathematical model.

Let the set of features present in the unknown sample X be G_X and the corresponding set in the reference G_R and let the intersection of G_X with G_R be the set G_{XR} , the set of the features the two compounds X and R have in common. The number of members in the three sets G_X , G_R , and G_{XR} shall be designated as T_X , T_R , and T_{XR} respectively. A very crude measure for the similarity between X and R is then given by T_{XR} . To normalize this result it is divided either by T_X or alternatively by T_R . In the first case, where the unknown sets the standard, the similarity becomes independent from the number of fea-

tures present in the reference only. Thus, the system does not penalize excess features in the reference. It just tries to make sure that the highest possible number of features present in X are also present in R. There is thus a tendency to retrieve references which are "too big". Each reference tries to represent all features of the unknown as completely as possible, the unknown tends to be a subset of the reference. This approach is referred to as a "forward search". It is particularly appropriate for similarity search of unknowns which can be assumed to be reasonably pure.

If the reference sets the standard, excess features in the unknown get along unpenalized. The system prefers references which are "too small". Each reference tries to be completely represented in the unknown, it tends to be a subset of the unknown. This strategy is referred to as "reverse search". It has its main application with samples suspected or known to be mixtures, because it gives the user a chance to identify components of the mixture.

Of course, forward and reverse search produce different results only if the spectra of the unknown and of the references are treated differently. If this is the case, a non-symmetrical similarity matrix results. The mathematical model given above is very much simplified. A more detailed analysis shows, that the resulting search strategy further depends on whether the case of a given feature being present in both spectra is valued differently from the case where the same feature is absent in both. If this is the case a non-symmetrical similarity matrix results even if the two spectra are not treated differently. At present, however, there is no method known to determine from the similarity matrix which search strategy is used by a given system. The only thing one can say is that systems producing a symmetrical similarity matrix either treat unknown and reference alike or use a balanced search strategy exactly halfway between the two extremes.

9. Outlook.

The philosophy behind any library search system for the interpretation of molecular spectra is based on the hypothesis, that similar spectra imply similar chemical structures. A library search system is useful in the real world of the analytical chemist only if it makes this hypothesis to become true. In order to build better library search systems, one needs similarity measures for both spectra and structures. The designer of a library search system decides upon the similarity for spectra. The similarity measure for structures, however, is defined by the user and depends on the problems he has to solve. In some cases he may be predominantly interested in references having the same functional groups as his unknowns and does not care a lot about the skeleton. In other applications, however, he may place main emphasis on the skeleton. Consequently there will never be one single and universally applicable similarity measure for chemical structures. Presently there is none at all. The designer of a library search system is therefore faced with the impossible job of optimally mapping a similarity measure for spectra onto an unknown and undefined similarity measure for structures. Currently he has no other choice than to rely on guesswork. The development of even a poorly performing similarity measure for chemical structures would allow for the application of formalized mathematical optimization methods and would almost immediately lead to better library search systems. Thus, future research in this field should concentrate on chemical structures rather than on spectra.

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The Use of Principal Component Analysis to Display PAH

Concentration Patterns in Indoor Air

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Abstract

Principal component analysis was used to display a data set consisting of the concentrations of fifteen polynuclear aromatic hydrocarbons (PAH) in indoor air. The data represented ten homes having different emission sources such as gas utilities, wood-burning fireplaces and cigarette smokers. The principal component analysis enabled convenient displays of the multidimensional data set from which characteristics of the PAH concentrations in the indoor air could be understood. The PAH concentration patterns of the indoor and the outdoor air were quite different even when air exchange rates were fairly high. Among the homes, different PAH concentration patterns emerged depending upon the emission sources present. Of the sources, cigarette smoking appeared to affect indoor air most adversely. The variable loading plots along with the correlation matrix were used to identify the interrelationships between the concentrations of PAH in indoor air.

Introduction

Most environmental monitoring studies involve measuring several pollutants simultaneously. Since the concentration of each pollutant is a variable (or a dimension), the resulting multidimensional data may be difficult to interpret. Multivariate statistical analysis can be used to interpret multidimensional data sets. Several such applications to a variety of environmental problems have been reported in the past few years (1-3). The objective of this study was to interpret a data set of PAH concentrations in indoor air using principal component analysis, which is an effective way of projecting multidimensional data onto two or three dimensions while preserving most of the variance in the data set (4).

Description of Data: The data were obtained from a study of indoor and outdoor air at homes in Columbus, OH (5). Stratification variables in the study were the following combustion sources: cigarette smoking, use of woodburning fireplaces, and heating and cooking by natural gas or electricity. Details of the sampling and analysis procedures have been published elsewhere (5). The fifteen PAH measured are listed in Table 1.

Data Analysis

The data matrix was formed by taking each PAH as a variable. Each row represented a PAH and each column a room (kitchen, living room or bedroom) in one of the homes. Since we were doing exploratory data analysis, none of the variables were rejected. To eliminate the unduly large effect of those variables that had large magnitudes, each variable was standardized so that it had a mean of zero and unit variance (4). The PCs were rotated using varimax rotation (4), to maximize the number of loadings that are either high or near zero and minimizes the loadings that have intermediate values (1). The univariate Pearson correlation coefficients were also calculated. For the data analysis, the statistical package Statgraphics (6) was used.

Results and Discussion

Effects of combustion sources

The results of the PC analysis for all the homes is presented in Figures 1A and 1B. The first two PCs accounted for 73.7% of the variance, of which PC1 contributed 61.8%. Figure 1A shows the variable loading plot, and Figure 1B shows the corresponding object score plot. Compounds 1,2 and 7-15 show high loadings along PC1. Of these, PAH 7-15 are collected primarily from the particulate phase. Some of the more volatile PAH 3,5 and 6, which are more abundant in the vapor phase, show low loadings on PC1 but high loadings on PC2.

The Pearson correlation coefficients also indicated strong correlations between the concentrations of PAH 3,5 and 6, evidenced by correlation coefficients close to 0.90. Fair correlations existed between PAH 7-15, those PAH that correlated strongly along PC1. Benzo[a]pyrene correlated strongly with PAH 9-14 (correlation coefficient close to 0.80). Concentrations of benzo[g,h,i]perylene (PAH 14) and coronene (PAH 15) are well-correlated.

In the object score plot Figure 1B, we see clustering for different types of homes. The all-electric homes (type E) are characterized by low values on both axes, reflecting low concentrations of all PAH. Clustering of homes with gas utilities and woodburning fireplaces (type C), homes with gas utilities only (type A) and the smokers' homes (type B and D) is also evident. Despite the facts that the homes in this study were in different neighborhoods, were of different ages and floor plans, and that the sampling was done on different days, the class separations for the homes with different stratification variables are fairly good.

As seen in Figure 1B, both gas utilities and fireplaces affect the PAH concentration in indoor air. Homes A and C show increased scores on both PC axes compared to the all-electric homes E. This implies a net increase of both types of PAH in these homes. In Figure 1B, the gas-heated homes that have fireplaces (C) show relatively lower loadings on PC1 than the ones that do not have fireplaces (A). This lower PAH concentration may be due to higher intrusion of relatively

cleaner outdoor air when the fireplaces were in operation. An increase in the concentration of pollutants correlated with PC2 is reasonable, because these more volatile PAH are generated in greater quantities than are the larger PAH during combustion of wood (7).

In Figure 1B, the most dramatic effect is seen for homes with smokers (type B and D). Smoking resulted in higher values for both PC1 and PC2, that is, it generated all PAH compounds and its effects were more significant than those of the other stratification variables. Other studies have also shown that cigarette smoke produces a wide range of PAH (8).

The univariate correlation coefficients between the PAH in nonsmokers' homes and the smokers' homes showed interesting trends. The three-ring PAH 3, 5 and 6 were well correlated in both cases. Notable were the correlations among PAH 7-15. In smokers' homes, there was fairly good correlation between PAH 7-15. PAH 12 had a correlation coefficient greater than 0.80 with all PAH 7-13, and PAH 14 and 15 were strongly correlated. For the nonsmokers' homes, the correlation between PAH 7-15 was much smaller. PAH 12 has high correlation with PAH 13 and 14 only. This absence of correlation among PAH 7-15 in nonsmokers' homes implied that they were produced from a variety of sources, whereas in smokers' homes they came mainly from the cigarette smoke. This indicated that cigarette smoke can be a major contributor of PAH 7-15 in indoor air. Similar conclusions were also drawn from the PC analysis of each subset.

Indoor/outdoor comparison: In the PC analysis of the outdoor and the indoor PAH concentrations, the outdoor samples clustered along PC1 and indicated that the PAH concentration pattern outdoors differed from that indoors. The indoor air showed much higher values on PC2, indicating higher concentrations of the smaller PAH (PAH 1, 3, 5, 6).

Migration of pollutants: When different rooms (kitchen, living rooms and bedrooms) were projected on the object score plot, the different rooms within a house had similar characteristics even though a particular activity may not have taken place there. For example, even if no cigarettes were smoked in the bedrooms in smokers' homes, the bedroom units still clustered with rooms of other smokers' homes. This implies that there is ample migration of pollutants within a house. However, the kitchen, living room and bedroom of a given home did not necessarily cluster together. Regardless of varying air exchange rates, each type of home maintained its PAH concentration pattern.

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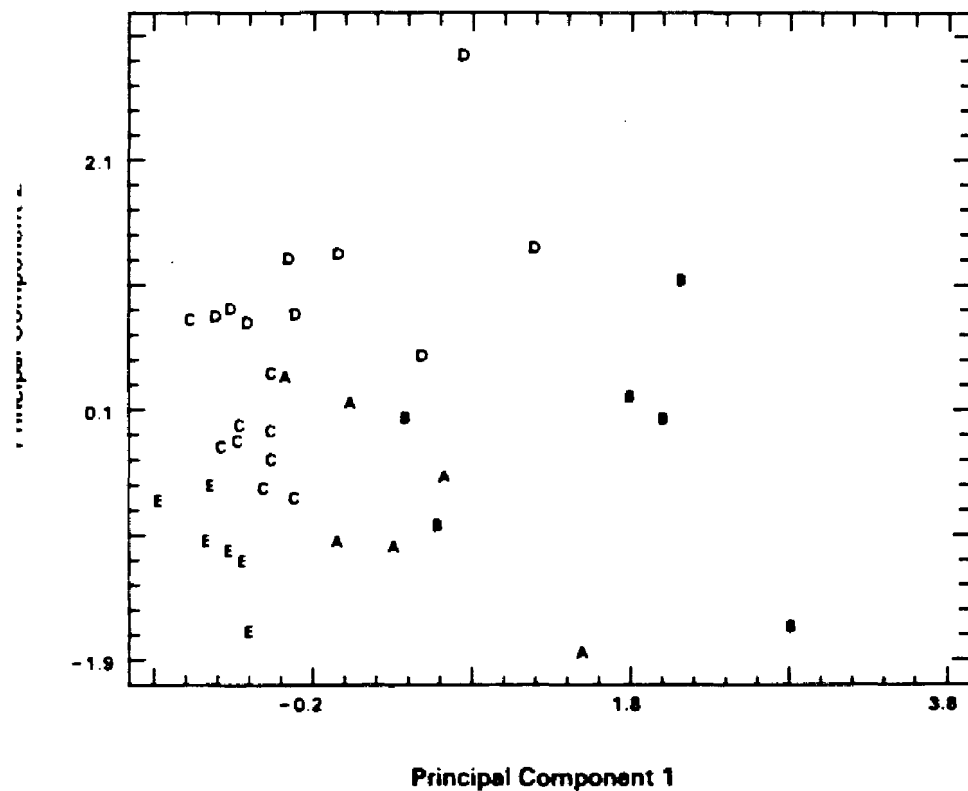
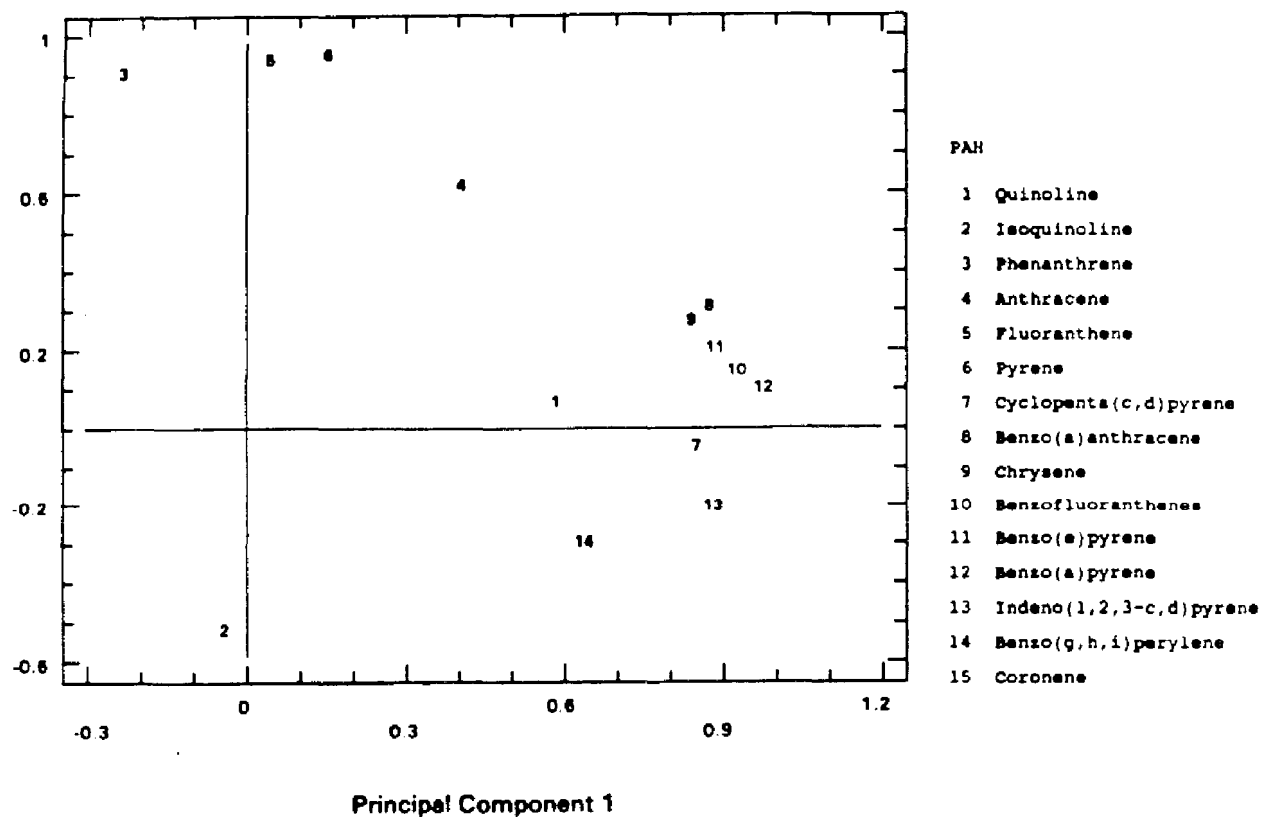


Figure 1. Principal component analysis of PAH in indoor air samples (kitchens and living rooms). (A) Variable loading plot, (B) Principal component score plot: A, homes with gas utilities; B, homes with gas utilities and smoking; C, homes with gas utilities and fire places in use; D, homes with gas utilities, smoking and fireplaces in use; E, all electric homes.

Statistical Modelling of Ambient Air Toxics Impacts During Remedial Investigations at a Landfill Site

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ABSTRACT

At landfills or other waste disposal sites, the off-site impacts due to air toxics generated by intrusive activities are a principal concern. To assess these impacts, the multivariate statistical technique of canonical correlation has been applied to ambient air toxics sampling data collected during a remedial investigation (RI) of a landfill in the metropolitan area of Los Angeles, CA. The goal of the analysis is to determine whether a site activity produces significant ambient air toxics impacts in the area immediately downwind of the site.

Canonical correlation analysis of the data collected at the downwind site reveals that the primary physical process occurring is dilution of contaminants by wind, with secondary slight increases in contaminant levels primarily due to boring activities. Although the canonical models are not strong enough for quantitative predictions for this data set, they do provide a realistic qualitative analysis of the physical situation.

INTRODUCTION

This paper presents the results obtained from application of canonical correlation analysis to ambient air toxics sampling data collected downwind of a landfill site during RI activities. Canonical correlation is a multivariate statistical technique that may be used to evaluate the relationship between groups of variables, in this case, meteorological conditions, site activities, and ambient air toxics levels. The technique is an extension of traditional multiple regression analysis, which seeks to relate a single variable to a group of other variables.

Canonical correlation was chosen as an analytical tool because of its ability to provide information beyond the scope of traditional statistical comparison techniques, such as simple tests for equality of means or multiple correlation. The use of multivariate methods allows better resolution of the complex interactions between the atmosphere and the variety of air toxics compounds that may be present due to intrusive activities on a landfill site.

SITE DESCRIPTION / DATA COLLECTION

The site was an urban landfill located in the Los Angeles area. The area is located to the northeast of the intersection of two major thoroughfares, with the upwind sampling site located near the

intersection. The downwind site is located beyond the northeast corner of the landfill area.

Ambient air samples were collected at the upwind and downwind locations during the 3-week site investigation. Wind speed and direction data were collected concurrently with the sampling periods. Due to the consistent land-sea breeze circulation pattern at the site, daytime winds were most frequently from the west-southwest. The upwind and downwind sampling locations were chosen based on this wind pattern.

During the activity period, a total of 31 high-volume air samples and 33 volatile organics samples were collected. The compounds detected included eight toxic volatile organic compounds (VOCs), copper, lead, zinc, and asbestos. The following eight VOCs were detected in at least 75% of the samples; acetone, benzene, ethylbenzene, styrene, toluene, xylenes, tetrachloroethene, and 1,1,1-trichloroethane.

The VOCs were collected using passivated stainless steel canisters (EPA Method TO-14), and the metals were analyzed from high-volume air samples of particulate matter. Asbestos was determined using low-volume personal pumps and filter cartridges.

Site activity was parameterized as the durations of the two principal intrusive activities: boring (soil core samples) and drilling (groundwater monitoring wells). Activity durations were obtained from the site log books.

UPWIND/DOWNWIND COMPARISONS

To assess the amount of contamination introduced into the ambient air by site activities, a comparison of upwind and downwind means may be used. Since normality is not a reasonable assumption for the air toxics data being considered, the t-test for equality of means was not used in the comparison. Instead, a nonparametric comparison of medians was performed using the Wilcoxon two-sample test for independent samples. None of the upwind/downwind pairs of medians were significantly different at the 10-percent level.

The upwind/downwind sample sets were also compared graphically using side-by-side box-and-whiskers plots, generated from descriptive statistics for the activity period. Figure 1 shows the data for several typical contaminants. There is a high degree of variability in the samples, and a characteristic skewing towards lower values.

These plots effectively portray the difficulty in determining whether the downwind contaminant levels are in any way distinctly greater than the upwind levels. Comparing means or medians would lead to the conclusion that site activities had no distinguishable impact on contaminant levels.

CANONICAL CORRELATION

Canonical correlation extends the sample correlation concept from two single variables to two sets of variables. The two sets are analogous to the dependent and independent variables in traditional regression

analysis. The canonical correlation procedure finds the most highly correlated pairs of linear combinations of the variables in each set. These linear combinations are known as canonical variable scores, and the sample correlation between a pair of scores is the canonical correlation coefficient. The scores may be interpreted by examining the component variables' sample correlations with the resultant score.

The canonical correlation procedure was performed based on the correlation matrix for the contaminant variables combined with the wind vector components, and the activity durations. Solid and volatile contaminants were treated separately. The northerly and easterly wind speed components were mean values covering the period from 0700-1700 L each day.

Solid Contaminants

A summary of the results of the canonical correlation analysis for the solid contaminants at the downwind site is shown on Table 1. The first two pairs of canonical variates are significant at the 10-percent level. This and other coefficients significant at the 10-percent level are underlined. Table 2 shows the correlations of these pairs of scores with their component variables.

The general relationship expressed by the correlations of the first pair of scores is lower contaminant levels and more southerly winds. Based on site geography, the southerly (i.e., positive northerly) component would contribute to transport away from the downwind site (dilution). Therefore, the first set of canonical variates appears to represent the general reduction of contaminant levels at the downwind site by dilution.

The second pair of variates reflects higher contaminant levels and longer boring periods, based on the correlations. There is also a relatively high correlation in the activity/wind score with winds having relatively lower easterly components. The mean wind vector direction from the 13 activity days is west-southwesterly, with a mean easterly component roughly 1.5 times the mean northerly component. Winds having lower easterly components would be more from the southwest. Southwest winds produce the greatest over-site fetch at the downwind sampling location. Therefore, the second pair of variates may be interpreted as reflecting a general elevation of contaminant levels at the downwind location during site activity with more across-site winds.

The logical extension of this analysis would be to attempt to predict the quantitative effects of varying levels of site activity on contaminant levels. Constructing such a model would require establishing a solid relationship between the variables and the scores. Unfortunately, the correlations are too weak to be of predictive value. However, the canonical correlation analysis does indicate that elevated contaminant levels are at least qualitatively associated with increased boring activity.

Volatile Organic Contaminants

The canonical correlation analysis of the VOCs indicated one significant pair of variates. However, no contaminants were significantly correlated with the contaminant score.

This type of ambiguity occurs in canonical correlation analyses whenever there are strong correlations between many variables in either group. Such a high degree of correlation does exist amongst many pairs of VOCs, principally due to the influence of nearby traffic emissions. The use of highly correlated predictor variables in linear regression produces an analogous effect. More definitive results may be possible if some of the highly correlated variables were eliminated.

CONCLUSIONS

Ambient air toxics data collected upwind and downwind of a landfill during intrusive activities were evaluated using basic statistical comparisons. Both side-by-side box plots and Wilcoxon two-sample tests for equal medians showed no significant differences in contaminant levels at the two sampling sites.

Canonical correlation analysis of the solid contaminant levels and the activity/wind variables at the downwind site shows that: 1) there is primarily dispersion of contaminants across the normal sea-breeze wind direction (southwest), and 2) boring duration and metals levels are positively related. These canonical relationships are not strong enough for quantitative use.

Canonical correlation analysis of the VOC data at the downwind site are rendered indeterminant due to a high degree of inter-correlation among the volatile contaminants. These interrelationships are mainly due to the source signature of traffic on the thoroughfares bordering the site, which likely obscures any relationships between VOC levels and site activity.

The use of canonical correlation to analyze data from air sampling efforts provided useful results in this case, beyond the information revealed by simple statistical comparisons. The results obtained were consistent with the expected physical process of dispersion. Although no quantitative judgments could be made from this data set, the method has the potential to provide quantitative results as well.

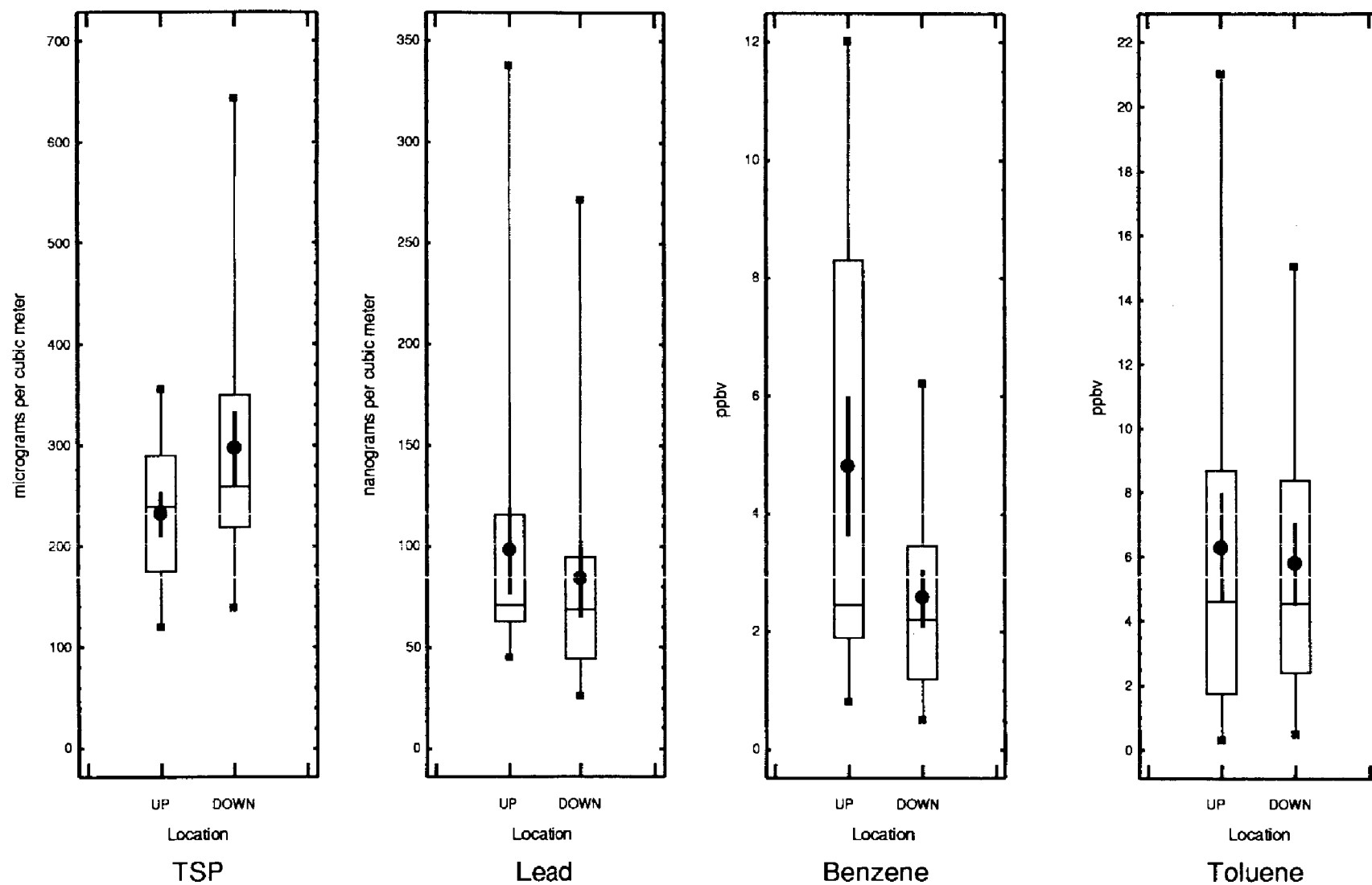


Figure 1. Typical box plots for activity period: dots and bars represent the mean and ± 1 standard error bounds.

TABLE 1. Canonical Correlation Results: Downwind, Solid Contaminants

COMPONENT NUMBER	CANONICAL CORRELATION	SIGNIFICANCE LEVEL
1	0.9715	0.0069
2	0.9027	0.0951
3	0.7421	0.3274
4	0.4159	0.5145

TABLE 2. Correlations of Scores with Original Variables

CONTAMINANT SCORE

VARIABLE	COMPONENT 1	COMPONENT 2
Asbestos	-0.427	-0.048
TSP	-0.170	0.228
Copper	<u>-0.511</u>	-0.190
Lead	-0.199	<u>0.669</u>
Zinc	0.122	0.467

WIND/ACTIVITY SCORE

VARIABLE	COMPONENT 1	COMPONENT 2
Northerly	<u>0.704</u>	0.248
Easterly	-0.061	-0.427
Boring	-0.209	<u>0.939</u>
Drilling	0.383	-0.150

**COMPARISON OF THE SOURCE LOCATIONS
AND THEIR SEASONAL PATTERNS FOR
SULFUR SPECIES IN PRECIPITATION
AND AMBIENT PARTICLES IN ONTARIO, CANADA**

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The Potential Source Contribution Function (PSCF) is a probability function based on the air parcel trajectory data coupled with information regarding the nature of the contaminants measured in that air parcel. PSCF is the ratio of the probability of a contaminated air parcel having traversed a 1° latitude by 1° longitude area to the probability that any air parcel traversed that area. Regions with high PSCF values thus have a higher probability of contributing pollutants to the measured concentrations at the receptor site. The PSCF analysis has been applied to sulfur species in both precipitation samples and particulate samples collected by Acidic Precipitation in Ontario Study (APIOS) network. Analysis has been performed separately for the winter and summer seasons so that the comparison between particles and precipitation and/or winter and summer can be made. The results show that the U.S. midwest, east coast, and nearby Atlantic Ocean region are source areas for sulfur species, both in precipitation and in ambient particles, at Dorset, Ontario, Canada. The influence of these regions on SO_4^{2-} level is stronger for the particles than for the precipitation, and much stronger in summer than in winter. However, the influence on SO_2 is much greater in winter due to its longer life time in winter. Ocean emissions play a significant role in summer owing to more biological and photochemical activities.

Introduction

The Potential Source Contribution Function (PSCF) has been introduced to indicate those geographical areas that have a high probability of being source areas of pollution events at a specific receptor site¹. The important feature of a PSCF analysis is the capability of geographically locating pollution sources whereas most commonly used receptor models² identify pollution sources by their chemical characteristics rather than their locations. It is obvious that the locations of airborne pollutant sources are important information for air quality management.

The PSCF method has been described by the authors³. A brief review is given here. In a PSCF analysis, both sample chemistry data and related meteorological data are needed. From meteorological data, air parcel back trajectories ending at a receptor site can be calculated with a trajectory model^{4,5}. The trajectory segment endpoint at particular time relative to a sample period starting time is given by longitude and latitude. To calculate PSCF, the whole geographic region covered by the trajectories is divided into 1° longitude by 1° latitude cells so that PSCF will be a function of longitude and latitude. The PSCF value for the ij -th cell is calculated by:

$$PSCF_{ij} = \frac{m_{ij}}{n_{ij}} \quad (1)$$

where m_{ij} represents number of endpoints that correspond to the trajectories that arrived at a receptor site with pollutant concentrations higher than some pre-specified value, and n_{ij} stand for the total number of endpoints that fall into the ij -th cell.

$PSCF_{ij}$ is the probability that an air mass with specified pollutant concentrations arrives at a receptor site after having been observed to reside in the ij -th cell. Cells containing pollutant sources will have high probabilities. Therefore, the PSCF will identify those source areas that have a potential to contribute to the high concentrations of contaminants observed at the receptor site¹.

Previously, the PSCF method was applied to the acidic precipitation chemistry data obtained from Acidic Precipitation in Ontario Study (APIOS) network. The source locations of the precipitation constituents were investigated in that study³. This paper will present a PSCF analysis of sulfur species in both precipitation and ambient particles collected by the APIOS network. The source locations of the species in precipitation and ambient particles will be compared. The seasonal patterns of such locations will be demonstrated. A better understanding of atmospheric processes regarding acidic deposition is achieved by these comparisons.

Data Description

The chemistry data of daily ambient particulate samples and event precipitation samples are taken from APIOS network data base⁶. This study only focuses on sulfur species (SO_4^{2-} and SO_2) at one site in the network, Dorset (station code 3011, see Figure 1). Two measurements for ambient particles were used: sulfate in $\mu\text{g SO}_4^{2-}/\text{m}^3$ and sulfur dioxide in $\mu\text{g SO}_2/\text{m}^3$. For precipitation, sulfate data were analyzed. Before calculating PSCF, the original SO_4^{2-} concentration (in $\text{mg SO}_4^{2-}/\text{l}$) was converted to SO_4^{2-} wet deposition (mg SO_4^{2-}) in a unit area by multiplying the concentration by the precipitation sample volume in liter. The purpose of this transformation is to eliminate the dilution effect caused by the differences in precipitation volume.

The samples used in this study were those collected from 1984 to 1986. After the data designated as unreliable were eliminated, the number of valid data points for precipitation

SO_4^{2-} , particulate SO_4^{2-} , and particulate SO_2 were 401, 992, and 986, respectively, and the average values of these variables are $0.993 \text{ mg SO}_4^{2-}$, $3.14 \text{ }\mu\text{g SO}_4^{2-}/\text{m}^3$, and $3.67 \text{ }\mu\text{g SO}_2/\text{m}^3$, respectively. These average values were used as the cut-off values in PSCF computation of corresponding species.

In order to investigate seasonal variation, the data set for each variable was divided into two subsets, one for winter (from November through April), another for summer (from May through October).

Air parcel back trajectories ending at Dorset have been calculated by Ontario Ministry of the Environment⁴. The trajectory data were provided in the form of a list of time intervals and coordinates of the trajectory segment endpoints for each trajectory. Trajectories using surface level data were calculated each day at 0:00, 6:00, 12:00, and 18:00 using 3 hour time intervals for 48 hours backward in time. In order to increase the resolution, a linear interpolation was performed to obtain 1 hour time interval trajectories. Thus for each 24 hour sample, 192 trajectory endpoints are available for the PSCF analysis.

Results and Discussion

Samples with a species deposition (for precipitation) or concentration (for particles) higher than the average value of this species are designated as polluted samples. The PSCF values can be calculated for each cell based on equation (1) where m_{ij} is the number of endpoints associated to these designated polluted samples and n_{ij} is the number of endpoints for all samples. The PSCF values then can be plotted on the map (Figures 2-4).

Before interpreting these probability plots, two facts should be brought into notice: 1) The cells near boundary of a figure usually have far less total number of endpoints. Therefore, the confidence level for the PSCF results in these cells is much lower than the confidence level in cells in interior. To be specific, the cells in interior usually have endpoints of 50~5,000 whereas the cells near the boundary, particularly on the west side, have 20 or fewer endpoints. The results representing the interior of these figures are statistically more significant. 2) Errors in a trajectory increase as the calculation proceeds back in time from a starting point (receptor site). In this study, the west side of the region is far from the Dorset site (Figure 1) so that the trajectories over these areas probably have greater errors.

Precipitation Data

Figure 2 is the PSCF plots based on wet deposition of SO_4^{2-} . It shows winter (a) and summer (b) patterns. For high SO_4^{2-} wet deposition events, the areas from Tennessee, Kentucky, and Indiana to the east coast and some areas in the Atlantic Ocean are the source areas. However, the influence of these areas in winter is much weaker than in summer [compare Figure 2 (a) and (b)]. In summer, the most of these areas have PSCF values higher than 0.6. Some cells in this region, particularly along the east coast and nearby ocean areas have PSCF values in the range of 0.8-1. This result indicates that the wide region of U.S. midwest and the east coast and some ocean areas have high probability of being the source areas for summer high SO_4^{2-} wet deposition at Dorset. Some areas around Missouri also show a strong effect. Considering the available emission inventory information and possible greater errors in trajectories over this region (as discussed in previous paragraph), we believe that these high PSCF value spots have been somewhat shifted from the areas between Missouri and Illinois (around St. Louis area) to the location shown in the figures.

It has been observed that the cells in the Atlantic Ocean off the east coast of the United States have high PSCF values in summer. It appears that the ocean becomes a significant source in summer when biological processes are very active and high temperature is favorable for these species to escape from the water. A important species transferred from

ocean to atmosphere is dimethylsulfide (DMS). The DMS emission from ocean is comparable in magnitude to the SO_2 emission from fossil-fuel burning⁷. DMS will react in atmosphere and produce SO_2 and other products. Reactions of DMS and OH radical significantly consume DMS and produce SO_2 ^{8,9}, especially during the summer when photochemical activity is high. Thus the combination of biogenic sulfur emissions and photochemical activity may be the cause for the summer high PSCF values. According to these figures, the effect from the ocean is negligible in winter. Another factor that could possibly cause this seasonal difference is difference of transport pathways in winter and summer. In order to investigate the pathways, all the trajectories over this region were reviewed. It was observed that even more trajectories passed through this ocean region in winter than in summer. Therefore, the difference appears to be due to the source intensity rather than lack of the transport pathway in winter.

Ambient Particulate Data

Two sulfur species have different seasonal variations (Figure 3 and 4). In summer, the midwest region, especially the Ohio River Valley, is very strong source areas for SO_4^{2-} at Dorset. However, the SO_2 level at Dorset is only slightly affected by the midwest region, and strong influence is from the Atlantic Ocean. Although sulfur compounds' sources (SO_2 emission) in the Midwest are similar in winter and summer, photochemical reactions are far more important in summer. SO_2 will be easily transformed to SO_4^{2-} so that the influence of the midwest sources is observed in form of SO_4^{2-} . Only limited amount of SO_2 remains in air when the air parcel reaches the receptor site. For similar reasons discussed in the previous subsection of precipitation, the ocean source can be seen in both SO_4^{2-} and SO_2 form and its influence on SO_2 is distinct. This result also suggests that SO_2 produced by ocean has longer life time than SO_2 emitted from industries. More oxidants and radicals in continental atmosphere and high temperature make SO_2 to easily transform whereas marine atmosphere is cleaner.

In winter, the midwest region has less influence on SO_4^{2-} (but it is still a strong source region) and a stronger influence on SO_2 because $\text{SO}_2 \rightarrow \text{SO}_4^{2-}$ transformation process is much slower in winter. The effect of the ocean is very limited in winter. It is also noticed that Sudbury area (see Figure 1), one of the largest SO_2 sources in North America, has some influence on the SO_2 level at Dorset in the winter [see Figure 4(a)]. This effect is not observed in summer because of the prevailing wind directions. No effect of Sudbury on SO_4^{2-} (particles or precipitation, Figures 3 and 2) at Dorset is observed. The stack emitting SO_2 at Sudbury is very high and the distance between Sudbury and Dorset is short (about 225km). There is only a limited probability that SO_2 from Sudbury can reach the ground at Dorset and there is not sufficient time for SO_2 to transform to SO_4^{2-} within that relatively short time period.

Comparison between Precipitation and Particles

The comparison between precipitation and particles can only be made for SO_4^{2-} (Figures 2 and 3). In general, U.S. midwest region has a greater influence on particles than on precipitation, especially in winter. In summer, the source areas for particles are concentrated in the Ohio River Valley region while more source areas for precipitation tend to be in the east coast and the region around Missouri and Illinois.

According to this comparison, the sulfate coming from the midwest tends to remain in particle phase. It does not efficiently participate in precipitation formation process and it is not efficiently removed by the precipitation because the sulfate particles are too small to be efficiently washed out. On the other hand, the species from ocean and the east coast seem more efficiently involved the precipitation process. However, we have difficulty to interpret the influence of western region (around Missouri) to the SO_4^{2-} in precipitation. For further

interpretation of this phenomenon, studies on meteorology and mechanism of cloud and precipitation are needed.

The trajectories used in this work are surface trajectories. When multilayer trajectories become available in future studies, we could expect more information that may be helpful in interpreting these results.

CONCLUSION

An area with large emission rate is not necessarily a source area of a pollutant at a specific receptor site because factors, such as meteorological condition, atmospheric chemical and physical processes, will determine the transport of the pollutant. With PSCF analysis, pollution source locations can be easily identified in sense of probabilities. The PSCF analysis has been applied to precipitation and particulate samples that is collected by APIOS network during 1984-86. The PSCF plots indicate the U.S. midwest, east coast, and nearby Atlantic Ocean region as source areas for sulfur species, both in precipitation and in ambient particles, at Dorset, Ontario, Canada. The SO_4^{2-} level in particles is affected by these regions more greatly than in precipitation. The influence on SO_4^{2-} is much weaker in winter than in summer. For SO_2 , it is much stronger in winter due to its longer life time in winter. The east coast, the ocean region, and the region around St. Louis are more responsible for the acidic species in precipitation whereas Ohio River Valley region is more responsible for the acidic species in the particles. Ocean emissions play a significant role in summer owing to more biological and photochemical activities. Sudbury, one of the most important source area in North America, only has significant impact to SO_2 level at Dorset in winter. These results should be taken into consideration when developing control strategies.

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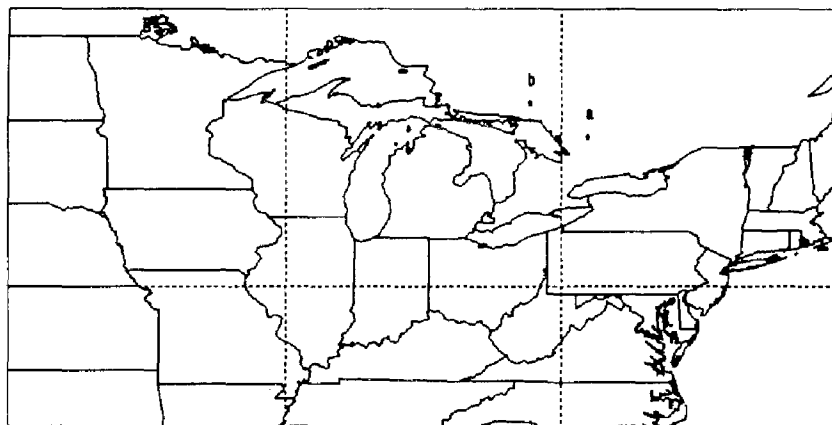
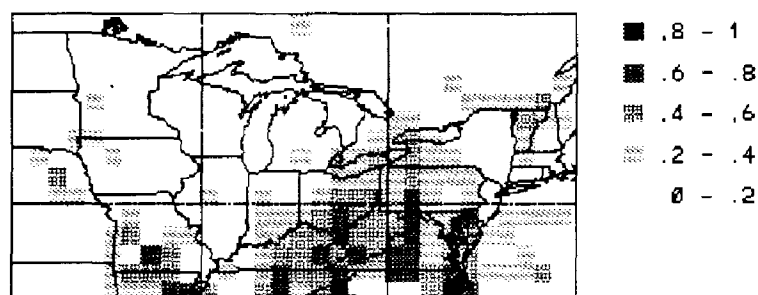


Figure 1 Map of studied region. a) Dorset, the receptor site; b) Sudbury, the biggest SO₂ point source in Canada.

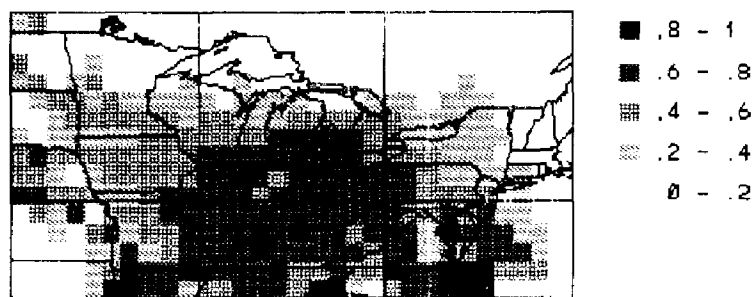


a. Winter.

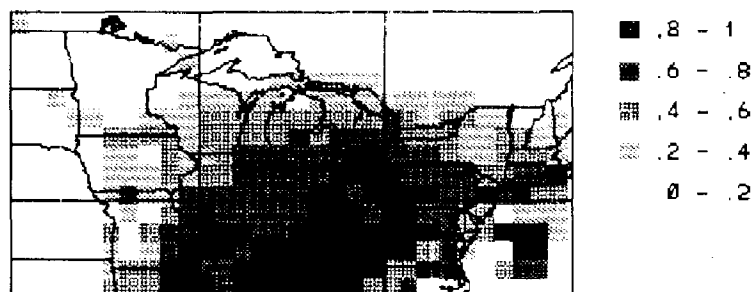


b. Summer.

Figure 2 PSCF based on SO₄²⁻ wet deposition.



a. Winter.

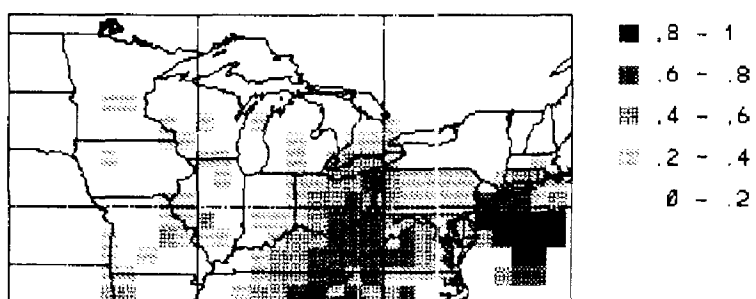


b. Summer.

Figure 3 PSCF based on ambient SO_4^{2-} concentration.



a. Winter.



b. Summer.

Figure 4 PSCF based on ambient SO_2 concentration.

MONITORING TOXIC VOCs IN URBAN AIR IN ILLINOIS

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Abstract

Toxic VOCs have been monitored at several sites in southeast Chicago and in the East St. Louis, IL metro area since 1987 using a canister-based sampling system. In both of these areas, toxic VOCs are emitted from a variety of area and point sources. Using wind trajectory analysis and chemical mass balance statistical methods, an attempt has been made to evaluate the effect of various types of emissions on overall levels of toxic VOCs in urban air. The data have also been analyzed to determine the influence of wind direction on concentrations of toxic VOCs in ambient air. In both study areas, major industrial point sources are responsible for occasional episodes with elevated concentrations of toxic VOCs. Average ambient concentrations, on the other hand, are influenced more by area sources that also affect regional background levels.

Introduction

Toxic volatile organic chemicals (VOCs) are recognized as important cancer risk factors in urban air.¹ Because these pollutants are emitted from such a wide variety of sources, identification and apportionment of individual chemicals among major sources is a complex problem. Other researchers have identified and characterized important sources of VOCs in urban areas.² VOCs can be apportioned among these sources using ambient air data with receptor modeling statistics³ or emissions inventory data and dispersion modeling.⁴ However, there is a high degree of uncertainty associated with these estimations due to uncertainties in emissions inventories, source profiles, meteorological variables and in the ambient air databases.

For the past three years, we have been monitoring ambient air in three industrialized urban areas and one rural background site in Illinois. The target compounds in this monitoring effort are a selected group of toxic aromatic and polychlorinated hydrocarbons that can be readily quantified in ambient air. To reduce the uncertainties associated with source apportionment by receptor modeling, we have used wind trajectory analysis, characterized site specific source profiles and incorporated regional background data. This approach is illustrated here using specific examples from our VOC monitoring data.

Methods

Samples and meteorological data were collected in East St. Louis and Granite City (part of the St. Louis metropolitan area) and in southeast Chicago. All three locations have typical urban sources as well as heavy industry (steel, chemicals, refineries and smelters). These areas have the worst air quality in Illinois in terms of criteria pollutants. Background samples were collected at a rural site near Champaign chosen to be representative of regional air quality.

The sampling and analytical methods used in this work and the results of quality assurance experiments have been described previously.⁵ Briefly, samples were automatically collected in stainless steel canisters using a commercially available sampler (SIS, Moscow, ID). VOCs are then analyzed using cryogenic preconcentration followed by capillary gas chromatography with flame ionization and electron capture detection. Complete meteorological data including wind speed and direction were collected with all samples.

EPA software⁶ was employed for the chemical mass balance (CMB) analysis. The chemicals analyzed were the toxic VOCs together with propane, n-butane and isopentane which were used as additional fitting species. Except where noted, source profiles are from Scheff et al.²

Results and Discussion

A data summary from approximately 250 analyses is presented in Table 1 for the 11 toxic compounds that were quantifiable in most samples. Even though the areas studied are heavily impacted by industrial sources, the average concentrations of toxic VOCs are similar to average urban values in the U.S.⁷ and are only 2 to 5 times higher than rural background levels in Illinois. The urban data are more variable than the rural data with maximum concentrations often more than ten times higher than the maximum levels seen at our rural background site. Typically the concentrations of toxic VOCs in urban areas approach rural levels except when the wind is blowing from a nearby major source.

This dependency on wind direction is shown in the data from one of our sites (Sauget) in the E. St. Louis area. This site is southeast of a large chemical manufacturing complex. This source affects the concentrations of several toxic VOCs in samples taken at this site during periods of steady (standard deviation of the wind direction < 20°) northwesterly winds (Table 2). A similar relationship is seen with benzene at the Chicago sites due to the influence of nearby coking operations. Used in this way, wind trajectory analysis (WTA) can verify the influence of inventoried point sources on air quality and confirm the presence and impact of uninventoried point sources.

Chemical mass balance (CMB) statistics were applied to a number of individual samples from the urban and rural background sites. A composite of VOC measurements taken at our rural site was developed as a regional profile. For East St. Louis, a chemical plant profile was developed by subtraction of simultaneous upwind from downwind fence line measurements.⁵

Prior to a detailed breakdown of the sources of individual compounds in the urban samples, some general findings are worth noting. CMB statistics for the rural samples are almost entirely accounted for by tailpipe emissions (67%) and gasoline vapors (19%) with a variety of other sources making up the remaining 15%. The urban samples tend to be highly variable even when comparing samples taken during periods of similar wind direction. For example, two East St. Louis samples were taken with winds coming from the chemical plant area. In one case, CMB indicated that the chemical plants accounted for 93% of the benzene; while in the other case, tailpipe emissions explained 100% of the benzene.

In Table 3 results are given for two CMB runs on a Chicago sample that reflected more or less average conditions at the site. The first indicates that a substantial portion of the chlorinated solvents are emitted from wastewater treatment. Although there is a sewage treatment plant in the study area, we have found no evidence from the emissions inventory, WTA or fence line sampling that this plant is a significant point source. Secondly, chloroform, an important indicator of wastewater treatment emissions, is no higher in this sample than in an average rural sample. In the second CMB run, a regional background signature is incorporated. This "source" accounts for most of the emissions. We interpret this to mean that most of the toxic VOCs in this sample come from the same sources as those contributing to the regional background. The additional compounds contributed by specific sources in the study area such as the coke ovens are highlighted in this example.

Table 4 gives the results of CMB analysis of a sample taken in East St. Louis that was strongly

influenced by chemical plant emissions. CMB accurately attributes some compounds (benzene for example) to the chemical plants. Others such as trichloroethylene (TCE) are attributed to other sources even though we know from WTA and fence-line sampling that the chemical plants are the dominant sources of TCE in this area. The overall statistics for this CMB run are not very good. This is probably due to the fact that the chemical plant profile is based on a limited number of grab samples. An improved profile would presumably give more accurate source attribution. Another point of interest in this CMB analysis is that gasoline vapors make up only a minor portion of toxic VOC emissions at this site even though petroleum product storage and transfer station emissions make up 70% of the point source hydrocarbon emissions inventory. This result agrees with WTA at the site (Table 2) in that levels of benzene, toluene and xylene are not elevated when the sampler is downwind of these sources.

Conclusions

1. The levels of airborne toxic VOCs in the study areas are strongly influenced by major point sources downwind of the sampler.
2. CMB analysis of VOC monitoring data can give misleading results due to uncertainties in source profiles and emissions inventories.
3. Wind trajectory analysis, specific source sampling and knowledge of regional background levels can provide important information for interpreting CMB results.

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Table 1. Toxic VOC concentrations in urban industrial areas^a

Compound	Chicago (n = 99)	E. St. Louis (n = 81)	Granite City (n = 24)	Rural Site (n=19)
benzene	4.2 ± 4.2 (26)	10.9 ± 17.5 (102)	2.3 ± 1.8 (7.5)	1.3 ± .5 (2.4)
toluene	9.1 ± 9.3 (56)	8.6 ± 9.5 (45)	6.0 ± 7.7 (40)	2.7 ± 2.0 (9.4)
m,p-xylene	3.9 ± 3.4 (21)	17 ± 43 (312)	4.2 ± 4.8 (24)	1.2 ± 0.8 (3.9)
ethylbenzene	1.4 ± 1.3 (7.6)	7.2 ± 17 (110)	1.6 ± 1.8 (7.4)	.5 ± .4 (1.6)
o-xylene	3.0 ± 5.7 (44)	3.4 ± 8.8 (55)	3.3 ± 3.8 (13)	1.1 ± 1.0 (4.3)
chloroform	0.3 ± 0.2 (1.6)	0.5 ± 0.9 (6.6)	0.3 ± 0.1 (0.5)	0.2 ± 0.1 (0.4)
1,1,1,trichloroethane	3.3 ± 3.6 (25)	4.0 ± 6.1 (31)	1.5 ± 1.6 (7.5)	1.2 0.4 (1.9)
carbon tetrachloride	0.8 ± 0.3 (1.7)	1.0 ± 0.4 (1.9)	0.7 ± 0.4 (1.8)	0.8 ± 0.3 (1.5)
trichloroethylene	1.0 ± 1.0 (5.9)	2.1 ± 5.8 (43)	0.6 ± 0.5 (2.1)	0.4 ± 0.3 (1.5)
tetrachloroethylene	1.8 ± 1.6 (9.1)	1.4 ± 1.3 (6.1)	0.6 ± 0.7 (3.3)	0.4 ± 0.3 (1.2)
chlorobenzene	0.3 ± 0.2 (1.5)	3.1 ± 6.4 (36)	0.4 ± 0.2 (0.7)	0.2 ± 0.1 (0.5)

^a Concentrations in $\mu\text{g}/\text{m}^3 \pm$ standard deviation, maximum value in parenthesis

Table 2. Wind trajectory analysis of Sauget/E. St. Louis VOC Data^a

Compound	Northwest Winds	Other Winds	Average
benzene	30 ± 8.0	2.2 ± 2.2*	14 ± 21
toluene	6 ± 6	9 ± 9	8 ± 8
m, p-xylene	52 ± 73	2.6 ± 2.2*	21 ± 50
trichloroethylene	5.9 ± 10	0.5 ± 0.5*	2.7 ± 7.0
chlorobenzene	5.9 ± 6.8	0.5 ± 0.4*	3.1 ± 5.4
p-dichlorobenzene	58 ± 61	3.0 ± 1.8*	38 ± 54

^a Concentrations are in $\mu\text{g}/\text{m}^3 \pm$ standard deviation, n=10 for each wind sector, * indicates values are significantly lower ($p > .95$) than other values in the same row.

Table 3. CMB results from Chicago (Washington School)

Date = 88/07/10
 Wind Direction = 225°
 Wind Speed = 13 mph

Fitting statistics

$R^2 = 0.97$ DF = 7
 $X^2 = 3.45$ Predicted Total Concentration
 of Fitting Elements = 96%

VOC	<u>Calculated Measured</u>	Tailpipe Emissions	Gasoline Vapors	Wastewater Treatment	Vapor Degreasing	Dry Cleaning
Benzene	0.84	81%	7%	11%	0%	0%
Toluene	0.96	71%	4%	26%	0%	0%
Ethylbenzene	1.05	82%	2%	16%	0%	0%
m,p-Xylene	1.03	96%	5%	n.a.	0%	0%
o-Xylene	0.67	98%	2%	n.a.	0%	0%
Chloroform	1.07	n.a.	n.a.	100%	0%	0%
Methylchloroform	0.75	n.a.	n.a.	38%	62%	0%
Trichloroethylene	1.19	n.a.	n.a.	27%	73%	0%
Perchloroethylene	1.00	n.a.	n.a.	37%	19%	44%

Date = 88/07/10
 Wind Direction = 225°
 Wind Speed = 13 mph

Fitting statistics

$R^2 = 0.99$ DF = 7
 $X^2 = 1.28$ Predicted Total Concentration
 of Fitting Elements = 98%

VOC	<u>Calculated Measured</u>	Coke Ovens	Gasoline Vapors	Architectural Coatings	Dry Cleaning	Regional Background
Benzene	0.98	38%	5%	0%	0%	56%
Toluene	1.02	0%	2%	44%	0%	53%
Ethylbenzene	0.96	4%	2%	7%	0%	86%
m,p-Xylene	0.99	2%	4%	15%	0%	79%
o-Xylene	0.98	0%	1%	18%	0%	81%
Chloroform	1.36	n.a.	n.a.	n.a.	0%	100%
Methylchloroform	0.81	n.a.	n.a.	n.a.	0%	100%
Trichloroethylene	0.84	n.a.	n.a.	n.a.	0%	100%
Perchloroethylene	1.00	n.a.	n.a.	n.a.	48%	52%

n.a. not available

Table 4. CMB results from East St. Louis (Sauget)

		<u>Fitting statistics</u>	
Date = 88/11/06		$R^2 = 0.90$	DF = 5
Wind Direction = 270°		$\chi^2 = 10.78$	Predicted Total Concentration of Fitting Elements = 101%

VOC	<u>Calculated Measured</u>	Tailpipe Emissions	Gasoline Vapors	Wastewater Treatment	Vapor Degreasing	Chemical Plant
Benzene	0.37	8%	2%	1%	0%	91%
Toluene	1.23	74%	8%	15%	0%	3%
Ethylbenzene	1.31	40%	2%	4%	0%	57%
m,p-Xylene	1.17	41%	4%	n.a.	0%	55%
o-Xylene	0.69	96%	4%	n.a.	0%	0%
Chloroform	0.84	n.a.	n.a.	40%	0%	59%
Methylchloroform	0.47	n.a.	n.a.	5%	52%	43%
Trichloroethylene	1.13	n.a.	n.a.	4%	72%	23%
Perchloroethylene	1.15	n.a.	n.a.	16%	49%	36%
Chlorobenzene	1.18	n.a.	n.a.	0%	0%	100%

n.a. not available

**CABIN AIR QUALITY: COTININE AS A BIOMARKER OF
ENVIRONMENTAL TOBACCO SMOKE IN COMMERCIAL
AIRCRAFT**

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The use of cotinine as a biomarker for evaluating air quality with respect to environmental tobacco smoke in commercial aircraft has been studied by determining the variation in concentration of nicotine and other environmental tobacco smoke pollutants in both smoking and nonsmoking cabin sections. Four never-smoker volunteers were exposed during commercial passenger flights and atmospheric samples were collected to determine exposure of the personnel to nicotine for at least the 24 hour period before and 48 hour period after the flight. Total urine samples were obtained from the personnel collecting the atmospheric samples for the time period extending from 24 hours before the flight to 48 hours after the flight. Exposure in airport terminals can be as significant as exposure for persons sitting a few rows in front of the smoking section during a flight. Urine cotinine concentrations were correlated with exposure to nicotine but not with exposure to many other constituents of environmental tobacco smoke in a series of DC-10 flights.

Introduction

In recent years there has been an increased interest in determining the concentrations of ETS in commercial aircraft passenger cabins in order to quantify the concentrations of pollutants associated with ETS which may be present, determine the factors which control the concentrations of ETS present in nonsmoking sections of passenger cabins, and develop models for predicting personal exposure in commercial aircraft. A National Academy of Sciences report (1) recommended banning smoking on all commercial flights for the following reasons: minimization of irritation, reduction of health risks and fire hazards, and to bring levels of pollutants in cabin air in line with those in other indoor environments. In April 1988, the U.S. Congress enacted a temporary law banning smoking on all flights of two hours or less. In February 1990, a new law went into effect which banned smoking on domestic U.S. airline flights. Similar legislation is in effect in Canada. Most flights in other countries do not presently ban smoking.

Several studies have determined the concentration of ETS components present in commercial aircraft cabins. Data have been reported on the concentrations of nicotine present in the cabin environment for a number of commercial aircraft flights (2-6). The exposure of airline flight attendants (4,7) and passengers (4) to environmental tobacco smoke has been estimated from measurements of nicotine and cotinine in urine. Oldaker et. al (2) have reported the determination of the concentrations of nicotine, RSP and UV-PM on several long commercial flights using a portable air sampling system. A similar sampling system was used to determine the concentrations of nicotine, CO and RSP at four locations in the passenger cabin of flights on MD-80 aircraft (5). The latter two studies are the only studies reported to date which have attempted to correlate the concentrations of nicotine in the passenger cabin of commercial aircraft with the concentrations of other constituents of environmental tobacco smoke. Most of the studies have used nicotine as the tracer to quantify exposure. However, exposure calculations based only on nicotine will underestimate total exposure to ETS since nicotine is removed from indoor environments at rates faster than other species associated with ETS (8,9).

We have conducted a study (10) to measure a variety of compounds associated with ETS as well as several non-unique species (such as RSP and CO) in both smoking and nonsmoking sections of aircraft cabins. The spectrum of species and aircraft sampled provided a data base for the development of models for the prediction of ETS concentrations in aircraft cabins under a variety of conditions. As part of that study, the concentrations of cotinine in the urine of passengers with known exposure to nicotine from environmental tobacco smoke before, during and after commercial flights was determined. This paper presents the results obtained from a series of DC-10 flights.

Methods

Sampling Equipment and Analysis Methods

Data on the aircraft were collected by four volunteers using Briefcase Automated Sampling Systems (BASS) (11). Each BASS contained various components designed to sample for specific compounds associated with ETS and other atmospheric pollutants and variables. Compounds measured during a flight included gas and particulate phase nicotine, 3-ethenylpyridine, fine ($>2.5\mu\text{m}$) particulate matter, UV-PM (2), NO_x and CO. The concentrations of gas and particulate phase nicotine were determined using two mini-annular denuder sections coated with benzenesulfonic acid (BSA) for collection of gas phase nicotine and 3-ethenylpyridine followed by a 1 micron Teflon

filter (Zefluor, Gelman Sciences) for collection and determination of nicotine (12). Following the Teflon filter was a BSA saturated filter for the collection of any nicotine lost from particles during sampling (12). Air was drawn through the denuder system at a rate of 2 sLpm. Details on the collection device used to measure the other chemical species have been given (10,11). The concentrations of nicotine to which the four volunteers were exposed in airports prior to and after each flight were determined using a filter pack with a 1 micron Teflon filter (Zefluor, Gelman Sciences) and a BSA saturated filter sampling at 4 sLpm for the collection of particulate and gas phase nicotine (12). The concentrations of nicotine present in the environment other than in the airport terminals and during the flight to which the volunteers were exposed was determined using a BSA saturated filter in a passive monitor of the design described by Hammond et al. (13).

A measured fraction of each urine void was collected by each of the four volunteers for the 24 hour period prior to and 48 hour period following each flight. Aliquots of the various samples were combined to give three composite 24 hour samples. After collection the individual urine samples were frozen and kept frozen at -80°C until combined to the 24 hour samples and analyzed.

Annular denuder and filter pack samples were extracted with water and analyzed by ion chromatography for nicotine and 3-ethenylpyridine (14) with the exception of the Teflon filter. The Teflon filter was extracted with methanol, with half of the extract analyzed for UV absorbance using a spectrophotometer to determine UV-PM (15), and the other half was analyzed for nicotine by ion chromatography (16). The concentrations of nicotine collected by the passive samplers was determined by gas chromatography using an NPD detector (12). Cotinine in the collected urine samples was determined by gas chromatography using an NPD detector and internal standard as previously described (14).

Sampling Protocol

Four different volunteer non-smokers participated in four DC-10 flights. Each subject carried a BASS and was seated in the rear passenger cabin which contained the economy class smoking section at the back of the aircraft. The location in the passenger cabin of the volunteers during each flight is given in Table I. Sampling was begun after takeoff when the no-smoking sign was turned off. Sampling was concluded when the no-smoking sign was turned on prior to landing. Flights 1 and 3 and flights 2 and 4 were the same origination and destination, however, a different DC-10 aircraft was flown for each flight. The four volunteers wore the personal passive sampler for a 24 hour period prior to the flight when not in an airport and were at the location of the filter pack sampling system when in an airport. After the flight, the volunteers were again in the area of the filter pack sampling system when in the airport and wore a passive sampler for the 48 hour period after leaving the airport. All volunteers stayed in smoke free residences and avoided any locations where smoking was present before and after each flight.

Results and Discussion

The concentrations of nicotine and the time duration of exposure for the four volunteers for the periods prior to, during, and after each of the four DC-10 flights are given in Table I. The concentrations given are for total nicotine determined using the annular denuder or filter pack sampling system, or of gaseous nicotine determined using the passive sampler. In all cases where both gas and particulate phase nicotine were determined, <95% of

the nicotine was in the gas phase.

The concentrations of nicotine and other selected environmental tobacco smoke constituents as a function of seat location in a flight with a high and moderate concentration of environmental tobacco smoke are given in Figure 1. Complete data for the four flights are available (10,17). The rate of penetration of environmental tobacco smoke constituents from the smoking section into the nonsmoking section follows a first order mechanism (10). The rate of penetration was the same for the various DC-10 aircraft flown in this study. The expected rate of decrease in the concentration of various constituents with distance into the nonsmoking section can be altered by selective removal of compounds by cabin surfaces (e.g. nicotine, Figure 1) or by the presence of non-ETS sources of some species in the nonsmoking section, e.g. CO, RSP or NO_x (10).

In some cases exposure of the four volunteers to environmental tobacco smoke in the airport terminal was significant, Table I. In all cases, exposure to environmental tobacco smoke other than in the aircraft cabin or in the airport terminals was insignificant. The airport terminal exposure concentrations are very low for the after flight data for Flights 1 and 3 and the before flight data for Flights 2 and 4 because of minimal smoking and the open air nature of the airport terminal. Because of the significant concentration present in the airport terminal and the longer waiting period before Flight 1, Subjects C and D on this flight were exposed to more nicotine in the airport terminal than during the flight even though they tried to avoid cigarette smoke in the terminal, Table I.

A total dose exposure to nicotine, Table II, was calculated for each of the subjects on each of the flights from the measured concentrations of nicotine in the airport terminals and during the flights, and the time of exposure at each location. An average tidal volume of 8.5 L/min (17) was used in these calculations. The total cotinine excreted in the 24 hour period before each flight and in the first two 24 hour periods after each flight are given in Table II. The calculated dose is compared to the 48 hr excreted cotinine in Figure 2.

The amount of cotinine excreted during the first (X_1) and second (X_2) 24-hr periods after each flight can be used to calculate the fraction of the total to be excreted present in the first 24-hr sample. This number was constant for all volunteers where X_2 was measurable, 0.84 ± 0.07 , except subject A in Flight 1. The cotinine elimination half time of 9 ± 2 hr agrees with the results of controlled exposure studies (14). Linear regression analysis of the data given in Figure 2 gives $r=0.78$ with a calculated slope of 0.13 ± 0.03 mol cotinine/mol nicotine. The slope is consistent with the expected conversion of about 10% of the inhaled nicotine to excreted cotinine (14). The large uncertainty in the slope apparently results from individual variations in nicotine metabolism, Table II. These variations result in an uncertainty of a factor of 2 in the use of urinary cotinine to predict exposure to nicotine. However, the more rapid removal of nicotine as compared to other constituents of environmental tobacco smoke in the cabin environment, Figure 1, results in larger errors in the use of cotinine to estimate exposure to these constituents. Such estimates are low by a factor of from 2-6 (10,17) for the data reported here.

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Table I. Concentrations of Total Nicotine from Environmental Tobacco Smoke to Which the Volunteers were Exposed Before, During and After Four DC-10 Flights.

Flight	Subject	Seat	Rows			
			Before Smoking		Total Nicotine, nmol/m ³ (Exposure Time, hr)	
			Section	In Airport	During Flight	In Airport
				Before Flight ^a		After Flight ^a
1	A	35D	0	58 (4.50) ^a	319 (4.87) ^b	>1 (1.20) ^a
	B	34G	0		208	
	C	32J	1		15.4	
	D	17D	16		0.1	
2	A	34C	0	>1 (1.0) ^a	84 (4.30) ^b	>1 (1.0) ^a
	B	33C	1		78	
	C	33A	1		39	
	D	24C	10		0.1	
3	A	32F	0	39 (1.87) ^a	475 (4.83) ^b	>1 (0.5) ^a
	B	31F	1		304	
	C	30D	2		127	
	D	26F	6		20.4	
4	A	35D	0	>1 (1.3) ^a	71 (4.55) ^b	13 (0.60) ^a
	B	33D	2		36	
	C	29C	6		12.2	
	D	24F	11		1.2	

^aBoth concentration and time were the same for all four volunteers.

^bTime was the same for all four volunteers.

Table II. Nicotine Exposure and Cotinine in Urine for Each of the Volunteers Involved in the DC-10 Flights.

Flight	Subject	Inhaled Nicotine nmol	% of Exposure During Flight	Total Urinary Cotinine, nmol			% of Inhaled Nicotine
				24 Hr Before Flight	0-24 Hr After Flight	24-48 Hr After Flight	
1	A	925	86	<3	144	66	22.7
	B	650	80	152 ^a	107 ^a	19 ^a	19.4
	C	171	22	NA ^b	NA ^b	NA ^b	NA
	D	133	0.2	<3	16	<3	11.9
2	A(C) ^c	184	100	NA ^b	NA ^b	NA ^b	NA
	B(B)	171	100	11		NA	NA
	C(A)	86	100				
	D(D)	0.2	100				
3	A	1207	97	<3	88	23	9.2
	B	786	95	<3	35	4	5.0
	C	350	89	<3	20	3	6.6
	D	87	57	<3	9	<3	9.9
4	A(C)	162	98				
	B(A)	88	95				
	C(B)	32	87	4	<3	<3	--
	D(D)	7	41	<3	3	<3	--

^aPreflight exposure to nicotine resulted from work in the analytical lab and not from ETS. Subsequent data have been corrected for this exposure assuming a constant elimination half life.

^bCotinine could not be determined due to nitrogen containing interfering compounds.

^cThe letter in () is the identification for this volunteer in the previous flight.

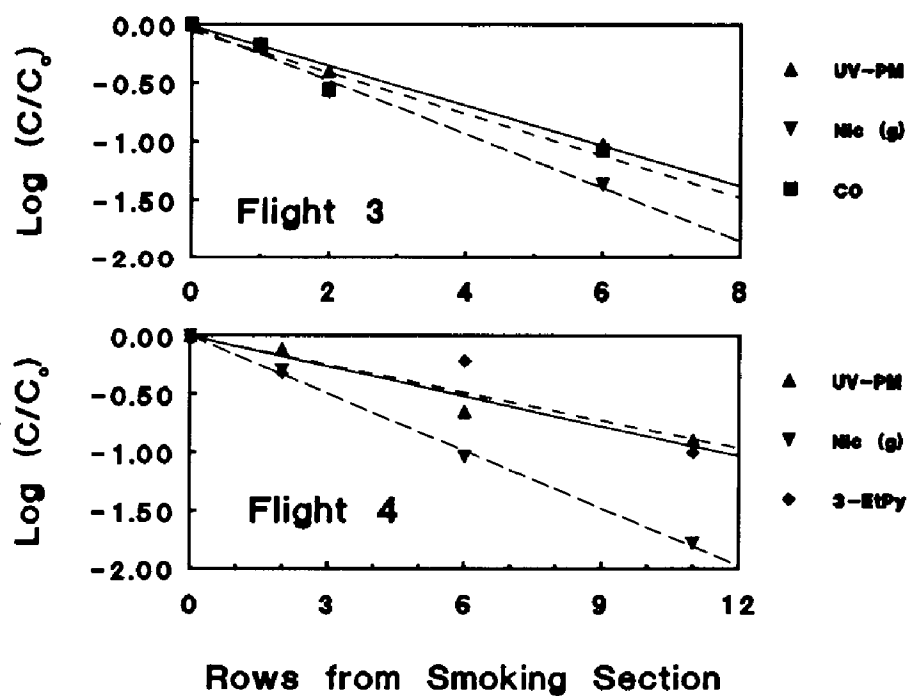


Figure 1. The $\log(C/C_0)$, where C_0 is the concentration in the smoking section, versus number of rows from the nonsmoking section into the smoking section for Flights 3 (high exposure) and 4 (moderate exposure).

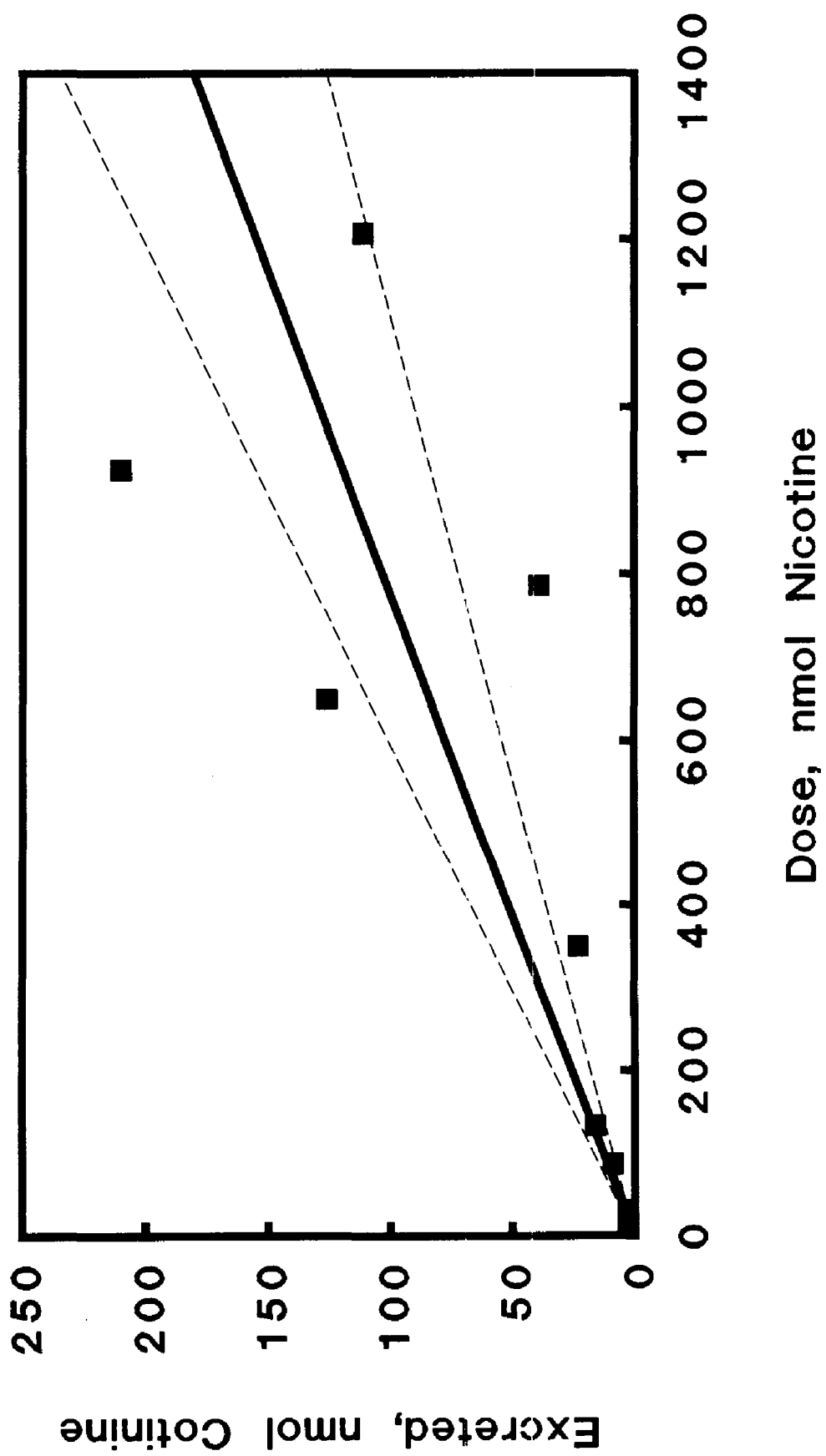


Figure 2. Total nicotine exposure vs cotinine excretion the 48 hours after the flight.

PROBLEMS WITH THE USE OF NICOTINE AS A PREDICTIVE ENVIRONMENTAL TOBACCO SMOKE MARKER

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A series of experiments was performed to evaluate the utility of nicotine as an environmental tobacco smoke (ETS) marker. Two University of Kentucky reference cigarettes (1R4F) were smoked in an 18-m³ environmental chamber. Air exchange rates within the chamber were varied from 0-4 air changes per hour, and the concentrations of numerous ETS components were monitored for up to six hours after smoking. Under most ventilation conditions, nicotine initially decayed more rapidly than other ETS constituents; however, as sampling time was extended, nicotine decayed more slowly. The change in nicotine decay rate can lead to overestimation of ETS exposure when nicotine is used as the sole ETS marker. Confirmatory results obtained from other field and chamber studies are also presented.

INTRODUCTION

The utility of nicotine as an environmental tobacco smoke (ETS) marker has been questioned by a number of investigators (1-3). Some have simply stated that it is a poor marker (1), while others have suggested that nicotine may underestimate ETS exposure (2,3) by as much as an order of magnitude.

The National Research Council (NRC) recommended that any chosen ETS marker should be present in a consistent ratio to ETS components of interest (4). To attain this criterion, the marker should possess the same decay characteristics as the component of interest.

If an ETS component is not generated or eliminated by chemical reaction, or does not interact with environmental surfaces, then it should demonstrate a first order decay with a rate constant proportional to the air exchange rate in a microenvironment. Previous studies have shown that nicotine does not undergo first order decay in microenvironments (2,3).

This present work was performed to systematically evaluate the effect of nicotine's unique decay on its ratio to other ETS components. Due to nicotine's different decay rate, both ventilation rate and sampling time would be expected to exert an effect on the ratio of nicotine to other ETS constituents. Therefore, ratios were determined at air exchange rates of 0, 0.5, 1, 2 and 4 air changes per hour (ACH), and time-weighted-average concentrations of selected analytes were determined for 0-30, 0-60, 0-120, 0-240, and 0-360 minutes following the smoking of 2 University of Kentucky reference cigarettes (1R4F). The results obtained in the chamber were then related to results obtained previously in field and chamber studies.

EXPERIMENTAL

Chamber Studies

All ETS decay experiments were performed in an 18-m³ environmental chamber described elsewhere (5). Three to five replicate experiments were performed at 0, 0.5, 1, 2, and 4 ACH. Real-time nicotine concentrations were monitored with a SCIEX TAGA 6000 tandem mass spectrometer (6). Real-time concentrations of carbon monoxide, nitrogen oxides, volatile organic compounds (estimated by FID response), and particle mass concentration were obtained with commercial analyzers described elsewhere (7). Vapor phase nicotine and 3-ethenylpyridine were collected using XAD-4 sorbent tubes and analyzed by gas chromatography with nitrogen phosphorus detection (8). Solanesol, gravimetric respirable suspended particles (RSP), ultraviolet particulate matter (UVP), and fluorescent particulate matter (FPM) were collected on Fluoropore filters and analyzed as described elsewhere (9,10). Duplicate nicotine and particulate samples were collected over the periods 0-30, 30-60, 60-120, 120-240, and 240-360 minutes, and integrated average concentrations were determined.

Each run during the decay rate studies lasted a total of 384 minutes. The first twelve minutes of the run were used to measure background concentrations of ETS constituents. A smoker then entered the chamber and smoked two University of Kentucky 1R4F cigarettes in 10½ minutes. The two cigarettes were lit at 30-second intervals, and the smoker took one puff on alternating cigarettes at one-minute intervals. Each cigarette lasted for an average of ten puffs. At 24 minutes, the smoker exited the chamber which was subsequently resealed for the final 360 minutes of the experiment.

The effect of residual nicotine on a smokers' clothing was determined from the average of 15 runs performed at various times over a three-month period in the environmental chamber which was operated at 0 ACH. After a twelve-minute background measurement, the smoker entered the chamber and stayed for twelve minutes. The smoker then exited the chamber, and nicotine concentration was monitored for an additional 36 minutes.

Field Studies

Nicotine samples were collected on XAD-4 sorbent tubes and analyzed by the method of Ogden *et al.* (8). Six-hour samples were collected in a smoker's van and the den of a non-smoker's house. Eight one-hour samples were collected overnight in a B767 aircraft which had completed a flight on which smoking was allowed.

Particulate samples were collected and analyzed for the aircraft study by the same methods used in the chamber study.

RESULTS AND DISCUSSION

Nicotine Decay

At each of the air exchange rates studied, nicotine initially decayed more rapidly than the other ETS constituents measured. However, at longer times the decay of nicotine slowed, and typically achieved a near-steady state concentration which was higher than the initial background level. On the other hand, constituents such as CO, volatile organic compounds, nitrogen oxides, and particle mass concentration decayed according to first order kinetics with decay rate constants which were proportional to the air exchange rate. The other constituents did decay to initial background levels in a time-scale consistent with normal first order decay.

A plot of nicotine concentration vs. time obtained from the average of five runs performed at 2 ACH is shown in Figure 1. The solid line in this figure is the average nicotine concentration measured in the chamber. The dashed line in the same figure is the nicotine concentration profile which would be predicted by first order decay.

The theoretical curve in Figure 1 is representative of the behavior of the other measured ETS constituents.

Time-weighted-average (TWA) concentration ratios between nicotine and the other constituents are proportional to the ratio of the areas under the two curves. For a sampling period extending from 0-30 minutes, the ratio of nicotine to analyte will be lower than that predicted by first order kinetics.

At about 30 minutes, nicotine decays less rapidly than the other constituents, and for sampling times greater than 60 minutes, the ratio of nicotine to other analytes will become increasingly larger than those predicted by first order decay of constituents. The magnitude of overestimation becomes larger if measurements are started at times long after smoking has occurred. For the example illustrated in Figure 1, the other constituents would have decayed to background at about 180 minutes; but significant concentrations of nicotine are still present in the chamber. In this case, a person exposed to the atmosphere in the chamber would not be exposed to measurable ETS particulate, CO, or volatile organic compounds, but they would have measurable exposure to nicotine.

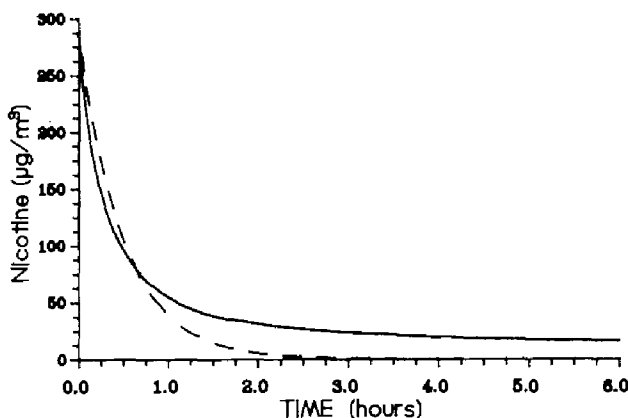
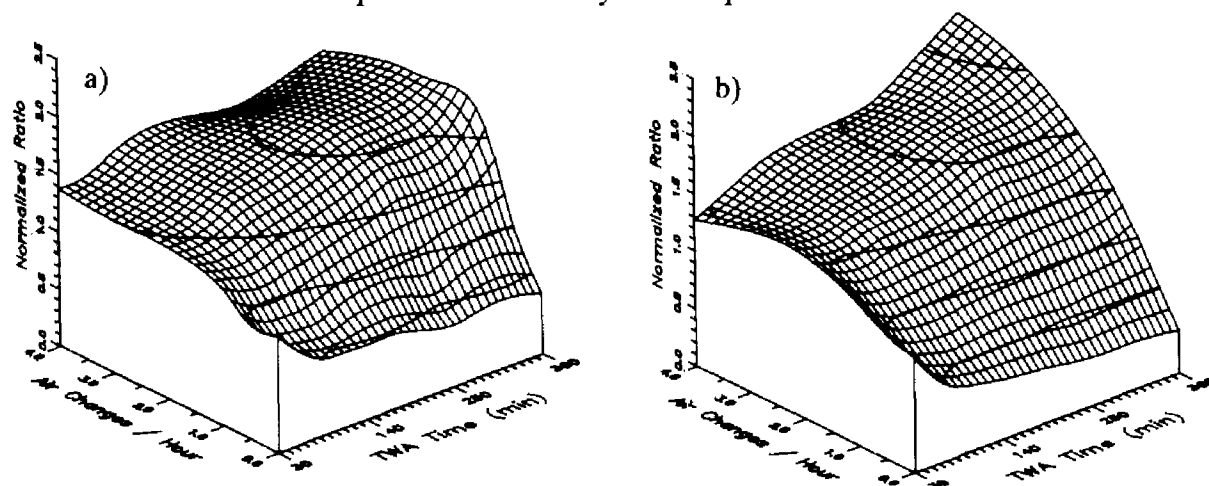


Figure 1. Average of five real-time nicotine concentrations (solid) measured in a controlled environment chamber operated at two ACH. The dashed line represents the concentration predicted by a first order decay mechanism.

Ratios Involving Nicotine

The actual variations of nicotine to RSP and nicotine to FID response ratios as a function of both sampling time and air exchange rate are shown in Figures 2a

and 2b. Ratios presented in these figures have been normalized to the values obtained for the 0-30 minute sample at 0 ACH. Sampling for increasing periods of time or sampling for a constant period of time at different air exchange rates has a dramatic influence on the observed ratio of nicotine to either vapor or particulate phase ETS components. Furthermore, these figures demonstrate that ratios of nicotine to other ETS components which are determined in chambers operated in static modes are not applicable to other environments because of the large overestimation of ETS exposure which they would predict.



Figures 2a & 2b. Normalized ratios between nicotine and gravimetric RSP (2a) and FID response (2b) as a function of both air exchange rate and sampling time. All values in figure 2a and 2b have been normalized to the ratio at 0 ACH and 30 min (0.108 in 2a & 74.1 in 2b). Lines of constant ratio are drawn at intervals of 0.333 beginning at a ratio of 0.667.

Field Measurements

Results consistent with those obtained in the chamber also have been observed in the field. Background nicotine concentrations in the absence of smoking have been measured in homes, automobiles and aircraft. In addition, nicotine desorption from the clothes and person of a smoker has been observed in the environmental chamber. Results of these studies suggest that the initial rapid decay of nicotine is due to its adsorption on clothing and other surfaces. As atmospheric nicotine is depleted, due to the effects of adsorption and dilution by fresh air, adsorbed nicotine then desorbs, and leads to measurable nicotine concentrations in the absence of smoking.

Figure 3 shows that smokers can be a source of nicotine contributed to the environment even when they are not smoking. This figure shows the average increase in nicotine concentration measured during 15 replicate experiments performed over a three-month period in which a smoker entered the environmental chamber for twelve minutes. The increased nicotine concentration is presumably due to the evolution of nicotine from the smoker's clothes. When the smoker exited the chamber, the nicotine concentration ceased its increase.

A nicotine concentration of $0.09 \mu\text{g}/\text{m}^3$ was measured in the den ($\approx 45 \text{ m}^3$) of a non-smoker's house. The sample was obtained two days after smoking had occurred in the room. This background level corresponds to small amounts of residual nicotine desorbing from room furnishings over a long period of time.

Nicotine samples were collected in a van ($\approx 5 \text{ m}^3$) in which smoking regularly

occurred. The sample was taken overnight and at least four hours after smoking had occurred in the vehicle. The sample was obtained at dashboard level ≈ 40 cm above an open ashtray. A background concentration of $0.126 \mu\text{g}/\text{m}^3$ was measured in the vehicle. Once again, this background is not due to the presence of ETS, but instead it comes from nicotine desorbing from the interior of the van and from cigarette butts present in the ashtray.

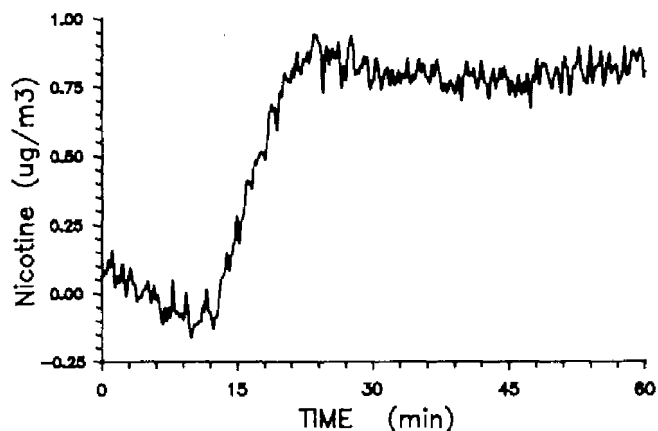


Figure 3. Average increase in nicotine concentration due to the nicotine desorption from a smoker's clothing in a controlled environment test chamber operated at 0 ACH. The smoker was in the chamber for the period 12-24 minutes.

Samples were also collected in a B767 aircraft in which smoking was permitted. The aircraft had returned from a regularly scheduled 4 hour 20 minute flight from Los Angeles, CA to Charlotte, NC. Samples were collected when the plane was on the ground and parked at the gate after all passengers and crew had left the plane. While the samples were collected, the aircraft was served by an auxiliary heating, ventilating and air conditioning system which provided fresh air at 13-26 ACH (11). Smoking was not permitted while the aircraft was at the gate, and none was observed. Samples were obtained in the coach smoking section and seats in the non-smoking border section. A total of 64 cigarette butts were counted in the ashtrays prior to sampling. The results of this investigation are presented in Table I. During time

period 4, the crew collected trash, emptied ashtrays during period 5, and vacuumed the cabin during period 7. UVPM measurements obtained from samples taken over the entire 8-hour period showed less than $1.5 \mu\text{g}/\text{m}^3$ particulate matter was present which could possibly be attributed to ETS. Once again, the only source of nicotine in the cabin would appear to be nicotine desorbing from interior surfaces

Table I. Background nicotine concentrations ($\mu\text{g}/\text{m}^3$) measured overnight on a B767 aircraft with auxillary ventilation. Smoking samples (S.) were obtained in the coach smoking section. Non-smoking samples (N.S.) were obtained in coach smoking/nonsmoking border seats.

<u>Sample</u>	<u>Time</u>	<u>Nicotine</u>	
		<u>S.</u>	<u>N.S.</u>
1	22:20-23:20	5.2	1.7
2	23:20-00:20	4.9	1.3
3	00:20-01:20	2.8	1.1
4	01:20-02:20	8.7	1.8
5	02:20-03:20	8.0	1.6
6	03:20-04:20	4.7	1.3
7	04:20-05:20	5.2	2.7
8	05:20-06:20	8.2	2.5

and cigarette butts. Measurable nicotine exposure could be expected in the non-smoking boundary section without concurrent exposure to ETS gas or particulate phase material.

CONCLUSIONS

Nicotine does not fit the NRC criteria for an ETS marker. The ratio of nicotine to other ETS constituents such as RSP are highly variable and dependent on both the air exchange rate at the sampling site and sampling time. Desorption of nicotine from clothing, interior surfaces, and cigarette butts leads to measurable nicotine exposure in the absence of ETS. The findings reported here show that when nicotine is used as the sole marker, it may greatly overestimate ETS exposure.

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POLYCYCLIC AROMATIC COMPOUND CONCENTRATIONS IN
RESIDENTIAL AIR ASSOCIATED WITH CIGARETTE SMOKING
AND GAS OR ELECTRIC HEATING AND COOKING SYSTEMS

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A small field study was conducted in Columbus, Ohio, during the winter of 1986-1987. Eight homes were selected for sampling on the basis of the following characteristics: electric/gas heating system, electric/gas cooking appliances, and absence/presence of environmental tobacco smoke (ETS). A 224 L/min sampler developed by Battelle was used indoors, and a PS-1 sampler was used outdoors. Sampler modules used both indoors and outdoors consisted of a quartz fiber filter in series with an XAD-4 trap to collect particles and semivolatile organic compounds. We measured 28 polycyclic aromatic hydrocarbons (PAH) and derivatives. The most abundant PAH found indoors and outdoors was naphthalene; the least abundant PAH was cyclopenta[c,d]pyrene. Higher average indoor concentrations of all but three target compounds were found when compared to outdoor levels. The presence of ETS in residential indoor air was identified as the most significant influence on indoor PAH and PAH derivative levels. Quinoline and isoquinoline concentrations correlated very well with nicotine concentrations and can be used as markers for indoor levels of ETS.

I. INTRODUCTION

Environmental tobacco smoke (ETS), which consists of sidestream smoke and exhaled mainstream smoke, has been considered as an important component of indoor air pollution. Many studies have shown that ETS can substantially increase the levels of mutagenicity, particulate matter, and polycyclic aromatic hydrocarbons (PAH) in indoor air (1-4). In most of the studies, indoor PAH concentrations were measured in test rooms with either smoking machines or smokers; the effects of ETS on indoor PAH levels in typical residences have not been fully investigated. The effects of ETS on residential indoor levels of PAH derivatives including nitro-PAH (NO₂-PAH), oxygenated PAH (OXY-PAH), and nitrogen heterocyclic compounds have not been reported. Among the PAH and their derivatives found in air, many compounds are mutagens or carcinogens (2,3,5,6). Human exposure to these pollutants in indoor air is of increasing concern because we spend approximately 80 percent of our time indoors (7).

A small pilot field study was conducted in eight homes in Columbus, Ohio, during the winter heating season of 1986/87 using the sampling and analysis methodology developed in our previous studies (9-19). The objective was to investigate the influence of several indoor pollution sources on the indoor pollutant levels. The indoor pollution sources included ETS, gas or electric furnaces, and gas or electric stoves. We measured 15 PAH, five NO₂-PAH, five OXY-PAH, and three nitrogen heterocyclic compounds.

II. EXPERIMENTAL METHODS

Sampling Methods

The homes were selected to give a large range of the number of cigarettes smoked. In addition, homes were selected so that nearly equal numbers of samples could be taken from each available combination of heating system and cooking appliance. At each home, two sequential 8-hr indoor samples were taken in the kitchen and living room using the quiet sampler (17). Single 16-hr outdoor samples were taken concurrently using a PS-1 sampler (General Metal Works, Cleves OH). Questionnaires describing the house characteristics, the ongoing activities in the house, and the sampling conditions were completed for each house by the field technician and the resident.

The sampling module consisted of a quartz fiber filter (104-mm QAST, Pallflex, Putnam CT) and XAD-4 (Supelco, Bellefonte PA) in series to collect both particle-bound and vapor-phase target compounds. We used XAD-4 in preference to XAD-2 in this study because of its better collection efficiency for nicotine (16). The detailed sampling procedures are described elsewhere (12). The air exchange rate of each house was determined from the gas chromatography/electron capture detector (GC/ECD) time profile of injected sulfur hexafluoride.

Analytical Method

The corresponding XAD-4 and filter samples were combined and extracted with dichloromethane (DCM) for 16 hr, then extracted with ethyl acetate (EAC)

for an additional 8 hr. The DCM and EAC extracts were combined and concentrated for subsequent chemical analysis.

Sample extracts were analyzed by gas chromatography/mass spectrometry (GC/MS) with positive chemical ionization (PCI) to determine PAH, quinoline, isoquinoline, and nicotine and by GC/MS with negative chemical ionization (NCI) to determine NO₂-PAH and OXY-PAH. A Finnigan 4500 quadrupole GC/MS system and an INCOS 2300 data system were employed. Methane was the reagent gas for both PCI and NCI, and compounds were ionized by a 150 eV electron beam. Peaks of target compounds monitored were the protonated molecular ion peaks for the PCI method and molecular ion peaks for the NCI method (12).

III. Results

The concentrations of the individual PAH measured ranged from 0.12 ng/m³ to 4,200 ng/m³. The most abundant PAH found in both indoor and outdoor air was naphthalene, and the least abundant PAH was cyclopenta[c,d]pyrene. The levels of NO₂-PAH and OXY-PAH were lower than those of their parent PAH. The highest indoor concentrations for all PAH and most of their derivatives were from home 5 during the living room sampling period (during which the highest number of cigarettes, a total of 20, was smoked).

When comparing the average concentrations in the three types of homes, we see that homes occupied by smokers had higher indoor concentrations of most target compounds than those from the same type of homes occupied by non-smokers. Thus, the presence of ETS appears to increase indoor levels of PAH and other pollutants.

Comparing the indoor concentrations over three types of homes occupied by nonsmokers, the homes having gas heating and cooking appliances had the highest average concentrations of most PAH compounds, followed by homes having gas heating and electric cooking appliances. Homes having electric heating and cooking appliances had the lowest concentrations of most PAH. However, the concentrations of PAH derivatives did not follow the same trend as those of PAH.

Higher average indoor levels were observed compared to the average outdoor levels for all but three PAH or derivatives (naphthalene, pyrene dicarboxylic acid anhydrides, and 2-nitrofluoranthene). For 2-nitrofluoranthene, the average outdoor level (0.06 ng/m³) was only slightly higher than the indoor level (0.05 ng/m³); for the other two PAH dicarboxylic acid anhydrides, the outdoor levels were approximately twice the indoor levels. In another study (13), we demonstrated that naphthalene and pyrene dicarboxylic acid anhydrides can be formed through the oxidation reactions of acenaphthylene and cyclopenta[c,d]pyrene with ultraviolet radiation or ozone. Therefore, higher outdoor concentrations of these compounds may arise from atmospheric reactions since higher ozone concentrations and ultraviolet radiation are expected outdoors. For the remaining target compounds, relatively lower outdoor concentrations are expected because there were no stationary contamination sources nearby, and local traffic was low in these residential areas.

Nicotine is a major component in ETS and has been used as a marker for ETS (20,21). Due to the large concentration ranges of nicotine among smokers' and nonsmokers' homes, we had to dilute some sample extracts and reanalyze them. We investigated the relationship among nicotine, quinoline, and isoquinoline to determine whether or not quinoline or isoquinoline can be used to monitor ETS more easily. Both quinoline and nicotine are found in cigarette smoke condensate. Quinoline has been reported to be the most abundant aza-arene in cigarette smoke and to be present at higher levels in sidestream smoke than in mainstream smoke (22). We used all the measured concentration levels across eight homes and three sampling locations to obtain a matrix of 75 Pearson correlation coefficients. The estimated correlation coefficients between nicotine and quinoline as well as nicotine and isoquinoline are 0.96 and 0.97, respectively. These results demonstrated that indoor concentrations of quinoline and isoquinoline correlate very well with those of nicotine. Based on this finding, we recommend the use of quinoline or isoquinoline instead of nicotine as an ETS marker for future field studies.

IV. Conclusions

The following conclusions can be drawn from this study:

- (1) The presence of ETS was the most significant contributor to indoor levels of PAH and most PAH derivatives.
- (2) Homes with gas heating systems were associated with higher pollutant levels, but the effect was not as important as the effect of ETS.
- (3) Quinoline and isoquinoline can be used as a marker for nicotine to measure residential indoor ETS levels.

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COMPARISON OF AREA AND PERSONAL SAMPLING METHODS FOR DETERMINING NICOTINE IN ENVIRONMENTAL TOBACCO SMOKE

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Nicotine in environmental tobacco smoke (ETS) was determined with portable air sampling systems (PASS's) and personal sampling devices to assess whether the two different methods give comparable estimates of exposure. Samples were collected with each method in 21 restaurants. For both methods nicotine is collected on XAD-4 resin and determined by gas chromatography with nitrogen selective detection. The mean nicotine concentrations determined by the PASS's and personal sampling devices were 6.3 and 4.3 $\mu\text{g}/\text{m}^3$, respectively. Results from a paired t-test and the Wilcoxon Signed Rank Test show that the PASS values are significantly higher than those of the personal sampling device: $P = 0.02$ and $P = 0.01$, respectively.

Introduction

The assessment of exposure to environmental tobacco smoke (ETS) is constrained by the absence of an easily determined, reliable indicator and by the need to collect samples unobtrusively. The portable air sampling system (PASS) represents one methodology used for assessing exposure to ETS (1). The PASS is used unobtrusively to determine both particle and gas phase indicators of ETS, the latter including nicotine. The PASS has been used in numerous surveys of ETS in several environmental categories including, for example, offices (2), restaurants (1, 2), and passenger cabins of commercial aircraft (3).

Because of obvious practical constraints, the PASS is applied as an area sampling method. Results from the PASS, therefore, might not be representative of personal exposures, which would be determined by use of personal sampling methods. The present study focuses on the determination of exposure to ETS nicotine. The objective of the study was to evaluate the comparability of results from determinations of ETS nicotine by the PASS and by personal sampling.

Experimental

Environmental Category

Samples were collected during September through December of 1989 in restaurants located in Greensboro, North Carolina. The restaurants represent a subset of a stratified, random population. The original population, selected for a survey performed in 1988 (1), was identified from the Dun and Bradstreet's Electronic Yellow Pages data base. Stratification was performed on the basis of restaurant styles including: "American Style, Fast Food,

Ethnic, and Other." This last designation includes, for example, "Barbecue Restaurants, Soda Shops, and Pizza Establishments." Two criteria observed for selecting restaurants were that seating be available for at least 50 diners and that there be no restrictions on smoking. The sample population for the 1989 survey had fewer restaurants than that of the 1988 survey because some restaurants went out of business and because some implemented smoking restrictions.

Sampling Locations

Sampling locations within restaurants were selected to conform as closely as possible to the guidelines described by Nagda and Rector (4) with the added constraint that samples be collected as close as possible to the same locations as for the 1988 survey. Samples were obtained with the PASS from locations between 0.6 and 1.8 m above the floor and at least 0.6 m from walls and other surfaces.

Sampling Procedures

All samples were collected for a minimum of one hour during the expected peak times for lunch. These times ranged from 11:30 a.m. to 1:00 p.m. and corresponded to those times when samples were collected for the 1988 survey.

Area samples for nicotine were obtained with the PASS. The nicotine collection system includes a constant flow sampling pump (SKC Inc., Eighty Four, PA) operated at a flow rate of 1 L/min, that is connected with rubber tubing to a sorbent tube containing XAD-4 resin (SKC Inc.). The inlet of the sorbent tube projects approximately 2 cm beyond the surface of the briefcase.

Personal samples for nicotine were collected with essentially the same equipment as used by the PASS. A constant flow sampling pump operating at 1 L/min was worn on the belt of the sampling team member, a rubber tube connected to the sorbent tube holder, and the XAD-4 sorbent tube was positioned within the breathing zone. With the exception of the XAD-4 sorbent tube and its holder, all other components of the personal sampling device were concealed under clothing.

In each restaurant, duplicate samples were collected concurrently with PASS's and personal sampling devices. During sample collection, sampling team members ate lunch and refrained from smoking.

Sampling pumps were calibrated with a film flow meter (Gilibrator, Gilian Inc.) before and after samples were collected. The mean flow rate was used to compute air volumes for those samples where calibration results showed a deviation less than 5%. For five samples, deviations greater than this value were observed; for these results the lower flow rate was used to compute sample volume, thus, giving an upper limit for the nicotine concentration.

Analytical Procedure

Nicotine was analyzed by the method described by Ogden *et al.* (5). XAD-4 sorbent tubes were extracted with ethyl acetate containing 0.01% (v/v) triethylamine. Analysis was performed by gas chromatography with nitrogen selective detection. Front and back sections of the sorbent tubes were analyzed separately to confirm the absence of breakthrough, of which none was observed.

RESULTS AND DISCUSSION

Table I presents the results from the determinations of nicotine with area sampling devices and personal sampling devices, which are identified "PASS" and "Personal," respectively. In addition, area and personal sampling results are identified by either "A" or "B." These designations show the pairing of sampling devices with each team member. Concentrations are in units of $\mu\text{g}/\text{m}^3$. Eight field blanks were analyzed with the PASS and personal samples; nicotine was not detected. One sample, associated with restaurant number 12 and PASS B, was lost.

Table II presents descriptive statistics for the nicotine concentration data. These statistics include arithmetic means, medians, minimum and maximum values, and number of samples. The arithmetic mean concentrations determined by the PASS's are greater than the corresponding concentrations determined by the personal sampling devices. With results pooled by sampling device, the mean concentration associated with the PASS's is $2.0 \mu\text{g}/\text{m}^3$ greater (46%) than that of the personal sampling devices.

Median nicotine concentrations are less than corresponding arithmetic mean concentrations, a relationship indicating that the distribution of the data is skewed toward higher concentrations. The median concentration results presented in Table II show a relationship between the PASS and the personal sampling devices that is quantitatively similar to that shown by the arithmetic mean concentration data. Thus, the median concentration determined by the PASS's is $1.3 \mu\text{g}/\text{m}^3$ greater (45%) than the median of the personal sampling devices.

The concentration ranges determined by the PASS's and personal sampling devices are similar. Concentration values span three orders of magnitude ranging from $0.3 \mu\text{g}/\text{m}^3$, just above the limit of detection, to approximately $25 \mu\text{g}/\text{m}^3$.

Statistical tests were performed to assess whether differences between concentrations determined by the PASS and personal sampling methods are significant. Data for each method and restaurant were averaged, because the sampling methods could not reasonably be assumed to be independent. (This approach is statistically more conservative with respect to detecting differences between the sampling methods.) Because environmental data are typically distributed log normally (6), Shapiro-Wilkes tests were done on raw and log transformed concentration data from the PASS and personal sampling devices. Results of these tests support a log normal distribution: for the PASS raw data, $P \leq 0.01$; for the personal raw data, $P \leq 0.01$; for the log transformed PASS data, $P = 0.41$; and for the log transformed personal data, $P = 0.97$.

A paired t-test was applied to the log transformed data to test for differences between the PASS and personal sampling methods. Results show that mean nicotine concentrations determined by PASS's are significantly greater than mean concentrations determined by personal sampling devices ($P = 0.02$). The same overall result is obtained when the data are evaluated with the Wilcoxon Signed Rank Test, a nonparametric statistical test. Thus, the results of this test show a statistically significant difference between mean concentrations determined by the PASS and personal sampling devices ($P = 0.01$).

Currently, we can only speculate on why there is a difference between the concentrations measured by the PASS and the personal sampling devices. We hypothesize that this difference reflects depletion of ETS nicotine at the

breathing zone relative to nicotine in the general air space sampled by the PASS. Adsorption of nicotine by fabrics and other surfaces at the breathing zone, as well as removal by human respiration, might account for such depletion.

CONCLUSIONS

Results from this investigation show that concentrations of ETS nicotine determined with the PASS, an area sampling device, are significantly greater than concentrations determined with personal sampling devices. This observed relationship indicates that results provided by the PASS in ETS surveys are conservative in their estimation of personal exposure to ETS nicotine.

Additional investigations need to be done to assess the relationships between PASS and personal determinations of other ETS indicators.

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Table I.

Results from Determinations of Nicotine with Area and Personal Sampling Devices in Restaurants

Restaurant Number	<u>Nicotine Concentration, $\mu\text{g}/\text{m}^3$</u>			
	<u>PASS</u>		<u>PERSONAL</u>	
	A	B	A	B
1	3.7	1.7	4.4	2.5
2	4.5	4.5	1.4	3.0
3	2.3	1.3	1.0	0.5
4	3.6	3.3	0.3	0.5
5	5.9	5.3	2.9	4.1
6	13.2	16.5	9.7	9.3
7	17.8	17.5	8.6	9.3
8	5.6	2.2	5.2	5.6
9	7.0	24.8	24.0	13.0
10	3.8	3.8	1.2	2.9
11	0.4	0.3	2.1	0.8
12	2.8	--*	0.3	0.9
13	4.2	4.8	4.2	1.9
14	5.9	6.2	1.8	1.2
15	7.6	9.8	5.6	7.6
16	1.4	1.7	1.5	2.9
17	3.8	4.0	3.0	3.4
18	10.8	7.3	6.1	4.1
19	1.2	1.3	1.3	1.3
20	2.9	2.7	2.6	1.9
21	15.9	13.8	13.4	4.2

* Sample lost.

Table II.

Descriptive Statistics for Area and Personal Sampling Results for Nicotine.

	<u>Nicotine Concentration, $\mu\text{g}/\text{m}^3$</u>					
	<u>PASS</u>			<u>Personal</u>		
	A	B	Pooled	A	B	Pooled
Mean	5.9	6.6	6.3	4.8	3.9	4.3
Median	4.2	4.2	4.2	2.9	2.9	2.9
Minimum	0.4	0.3	0.3	0.3	0.5	0.3
Maximum	17.8	24.8	24.8	24.0	13.0	24.0
<hr/>						
N	21	20	41	21	21	42

THE IMPACT OF CIGARETTE SMOKING ON
INDOOR AEROSOL MASS AND ELEMENTAL CONCENTRATIONS

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An indoor air quality study was conducted in two New York counties during the period of January 6 through April 15, 1986. Suffolk County is located on eastern Long Island, east of New York City. Onondaga County is situated in northwestern New York State and includes the city of Syracuse. Week long fine particle mass samples were collected indoors and outdoors of 394 homes. The homes were selected according to their potential indoor aerosol sources such as cigarette smoke, gas stoves, and heating sources. In this paper two home groups were selected to examine the impacts of cigarette smoke on the fine aerosol mass and elemental concentrations. These two data sets were created by removing all samples taken in homes with one or more indoor sources such as kerosene heaters, wood stoves, or fire places. For each of the counties, the remaining homes were divided into two groups: homes with smokers and homes without smokers. A simple comparison of average mass and elemental concentrations between smoking and non-smoking homes in each county enabled us to determine the elemental profile of cigarette smoke. Finally, the room to room variations in indoor concentrations were studied. The results of this analysis showed that all elements, including those associated with cigarette smoke, presented the same concentrations in the kitchen, living room, or other living areas.

Introduction

During the period of January 6 and April 15, 1986, an extensive indoor air quality program was conducted in Onondaga County and Suffolk County, in New York State. Suffolk County is located on eastern Long Island, east of New York City. Onondaga County is situated in northwestern New York State and includes the city of Syracuse. Week long fine particle mass samples were collected indoors in a total of 394 homes. The homes were selected according to their potential indoor aerosol sources such as cigarette smokers, gas stoves, wood burning, and kerosene heaters. Comparisons of indoor aerosol mass and elemental concentrations between homes with and homes without smokers will allow us to determine the elemental profiles of cigarette smoke emissions and determine their relative importance. Also in this paper we examine whether room to room differences in elemental concentrations exist. These comparisons included elements associated with cigarette smoke and elements associated with other indoor and outdoor sources.

Sampling and Analysis

The fine particle mass measurements were obtained using the Harvard Impactor which collects fine particles with aerodynamic diameters $< 2.5\mu\text{m}$ at a flow rate of 4 lpm^1 . A silent pumping unit was specially designed for indoor use. For single sample homes, the optimal sampling duration was 168 hours, or seven days. For homes with more than one sampling location, a time share unit with a solenoid system was installed on the pumping system to sample alternately for a fifteen minute period at each home location. Thus, these filters sampled for a total of 84 hours, approximately.

The fine particle mass collected on Teflon filters was gravimetrically determined using a Cahn balance. Subsequently, concentrations of elements associated with fine mass were determined by X-ray fluorescence (XRF): Al, Si, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Br, Sn, Sb, Ba, La, Cd, Pb. Among the above elements, Al, Ti, Cr, Sn, Sb, Ba, and La, presented a high percentage of concentrations below the detection limits; therefore they will not be examined.

In suburban Suffolk County, sampling was conducted from January 6 to February 24, 1986 in 194 residences resulting in 260 indoor and 20 outdoor samples. Indoor monitoring occurred in the living area of 187 homes. Monitoring commenced in approximately five different homes each day for an optimal duration of seven consecutive days throughout the study period. A subgroup of 73 homes had additional samplers placed in several rooms to examine

the room to room variation in aerosol mass and elemental concentrations. Onondaga County, a suburban-rural area, was sampled between February 24 and April 15, 1986. A total of 279 indoor and 37 outdoor samples were taken under the same sampling design in 200 residences. A subgroup of 83 homes had samples measured in rooms other than the living area.

Telephone interviews were conducted to poll prospective participants for the study. Questions concerning the presence and typical usage of indoor air pollution sources such as gas stoves, wood stoves or fireplaces, kerosene heaters, and smokers allowed for a preliminary stratification of the homes using a predetermined minimal source usage level. Information was also gathered on housing characteristics such as volume and air exchange rates. A diary of actual source usage such as minutes of gas stove use, total cigarettes smoked, and hours of kerosene burner, wood stove or fireplace use was kept by the participants in order to reclassify the homes based on actual source usage, again using minimal source usage rates. A comparison of the original strata and the actual strata suggests 49% of the Suffolk homes and 55% of the Onondaga homes were misclassified when relying solely on the telephone interview. This shows the importance of gathering actual source usage information for the specific sampling period. Although a predetermined minimal source usage level is appropriate for screening participants, when describing and assessing the impact of a source on the indoor environment an absolute criteria is necessary. Thus, for the purpose of this paper, any use of a source requires inclusion in that source category. Table 1 gives the mean and standard deviation of these source usage variables for Suffolk and Onondaga Counties. The table shows that more cigarettes were smoked in Suffolk, yet cigars and pipes were smoked more in Onondaga. Table 1 also gives a summary of the air exchange rates and house volumes for all homes. The average air exchange rates were similar for both counties however Suffolk homes showed more variability, 0.42 versus 0.27 per hour. House volumes were comparable on average yet the standard deviations of these measurements showed Onondaga almost twice as variable as Suffolk, suggesting varied housing stock.

Most sampling occurred in the living area of each home, defined as the room where the families spent most of their time. In addition, kitchens were monitored in 58 Suffolk homes and 62 Onondaga homes. In some instances, the family room, living room, or some other room was also sampled, however, these homes also had samples collected in the main living area. Lastly 19 valid outdoor samples were measured in Suffolk and 36 in Onondaga. These data were analyzed for room to room variation in aerosol concentrations and presented below. However, in describing the

distribution of elemental concentrations for various source categories, only the living area samples were included so as not to bias the estimates toward the multiple sample homes, and also because the room to room variation analysis supported this approach as shown below.

Results and Discussion

To investigate differences in fine aerosol mass and elemental concentrations between homes with and without smokers, a subset of homes was selected. This subset includes homes, from both counties, in which major indoor sources such as kerosene heaters, wood stoves and fireplaces are not present. Subsequently, these two data sets, one per county, were further separated into groups. The first group includes homes without smokers, and the second includes homes with smokers. Note that both smoking and non-smoking home groups include gas stove use, since previous analysis of this data has shown that gas stove use did not contribute to indoor aerosol mass and elemental concentrations. Thus this source was not considered for the above home classification. Tables 2a and 2b depict the calculated geometric mean and standard deviation of mass and elemental concentrations for non-smoking homes, smoking homes, and outdoors, for Suffolk and Onondaga Counties, respectively.

For both counties, the average indoor fine mass concentration in no smoking homes and the outdoor concentration exhibit similar levels. Since not all outdoor soil particles penetrate the indoor environment, these results suggest the presence of indoor sources. In fact, some activities such as showering, vacuuming, cooking, or biological aerosols generated indoors could contribute to indoor fine mass. Furthermore, for both counties, fine mass concentrations were considerably higher in homes with smokers than homes with no smokers. For Suffolk and Onondaga the respective concentrations were 17.3 versus 49.3 $\mu\text{g}/\text{m}^3$ and 14.4 versus 36.5 $\mu\text{g}/\text{m}^3$, respectively. Thus, homes with smokers present mass concentrations which are approximately three times higher than homes with no smokers.

The results of Tables 2a and 2b suggest that chloride and potassium concentrations in homes with no smokers are associated with indoor as well as outdoor sources. For non-smoking homes, chloride levels are approximately two times higher than the outdoor concentration. High chloride concentrations in non-smoking homes have been observed in previous indoor air quality studies and were attributed to the use of consumer products ^{2,3}. For homes with smokers, the chloride levels were much higher, five to eight times the outdoor concentration. Moreover, for non-smoking homes, indoor potassium concentrations

were found to exhibit similar levels to those observed outdoors in both Suffolk and Onondaga County, as shown by Tables 2a and 2b, respectively. Potassium is mostly associated with soil particles in the non-smoking homes. However, for the case of smoking homes, potassium levels can be five to six times the outdoor concentration. These results are in good agreement with findings reported by Santanam and Spengler ⁴.

Cadmium and to a lesser extent bromine are also associated with cigarette smoke emissions. Indoor cadmium concentrations were similar to those observed outdoors, suggesting the presence of a minor indoor source. However, there is no information about the existence of indoor cadmium sources in exception to cigarette smoking ⁵. In fact, homes with smokers presented concentrations which are two to three times higher than outdoors, suggesting that cigarette emissions contain cadmium. Of course, the contribution of smoking to indoor cadmium concentrations will depend on, among other things, the number of cigarettes smoked and the type of tobacco used. Similarly, it has been found that in homes with no smokers, bromine concentrations were lower than outdoors suggesting that this element is mostly related to outdoor sources; that is, automobile emissions. However, for homes with smokers, bromine showed slightly higher concentrations than outdoors providing some evidence that indoor bromine is associated with this source.

Finally, Tables 2a and 2b suggest that the rest of the analyzed elements are not associated with cigarette smoke in Suffolk and Onondaga Counties, respectively. Among them S, V, Mn, Fe, Ni, Se, and Pb, and to a lesser extent Si, Zn, and As are mostly related with outdoor sources. The rest of the elements, Ca and Cu have significant indoor sources.

Furthermore, we investigated room to room variation of fine particle mass and elemental concentrations. More precisely, mass and elemental concentrations obtained from samples collected at locations other than the living area, such as kitchen, family room, or other living space were collocated with samples from the living area. Since some of the analyzed elements are cigarette smoke tracers, such as Cl and K, as shown above, the room to room variation provides us with great insight into the source emission distribution.

The sample design dictated that the analysis be separated into kitchen versus living area, and other living space versus living area with other living space defined as any sample location other than the kitchen. Mass and elemental concentrations measured in these rooms were regressed on the corresponding living area concentrations. The regression results of mass and all elements are shown in Table 3 for the kitchen and

living area analysis. This analysis includes homes with no smokers for both Suffolk and Onondaga counties. Coefficients which are not statistically significant are marked with an asterisk. The regression results suggest that the mass, Si, S, Cl, K, Ca, V, Mn, Fe, Ni, Cu, Zn, Br and Pb concentrations in the kitchen can be predicted satisfactorily from those measured in the living room. For Cd, As, and to a lesser extent, Se, the regression results are not satisfactory. This is due to the fact that X-ray fluorescence is unable to determine precisely the concentrations of these elements in the nanogram level. As can be seen by these results, fine aerosols are well mixed in the indoor environment, as shown previously by Ju and Spengler ⁶. Of course, this happens because the characteristic time of fine particle mixing within the home is significantly shorter than the sampling period. Room to room elemental aerosol profile variations were also examined by comparing living area concentrations to other living space concentrations. The results of the regression analysis suggested that elemental concentrations in other living spaces can be estimated using those measured in the living area. Again for Cd, Se, and As and to a lesser extent, Ni and Cu, the correlation coefficients were very low, reflecting the high analytical uncertainties. These relationships are similar to those obtained for the kitchen/living area comparison. Finally, a similar analysis was conducted for only homes with smokers. The results of these analyses, shown in Table 4, reveal the same relationship for all location comparisons, suggesting no need for further analysis by home category.

Using a nonparametric analysis of variance we again examined the assumption that fine aerosols are well mixed within a home. For this test the hypothesis is that the concentrations in the kitchen are similar to those in the living area. Concentrations of fine mass and all elements are not significantly different in the kitchen or living area, at the $p=.05$ level. The same hypothesis was posed for living area versus other living space locations. The results also confirm no significant difference between these rooms for any element except Se. In conclusion, the above comparisons reveal that a single sampling location is enough to assess indoor human exposure to fine aerosols.

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Table 1 Summary of source usage data and home characteristics.

Variable	SUFFOLK			ONONDAGA		
	N	Mean	Std	N	Mean	Std
Cigarettes (# smoked)	130	113.4	136.1	120	85.2	90.9
Cigars (# smoked)	2	10.5	13.4	3	20.0	24.3
Pipefuls (# smoked)	4	5.5	5.1	10	10.1	12.6
Air Changes (per hr)	189	0.58	0.42	197	0.50	0.27
House Volume (ft ³)	193	12441	5852	200	12470	8954

Table 2a Geometric means and standard deviations of mass ($\mu\text{g}/\text{m}^3$) and elemental (ng/m^3) concentrations in Suffolk County.

Element	Non-Smoking		Smoking		Outdoors	
	Mean	σ	Mean	σ	Mean	σ
Mass	17.3	1.7	49.3	1.8	16.9	1.3
Si	82.8	2.1	90.3	3.3	88.4	1.3
S	1224.1	1.6	1161.1	1.7	1779.1	1.4
Cl	37.4	2.6	197.2	2.9	21.3	1.4
K	86.6	2.2	431.5	2.4	71.3	1.5
Ca	39.5	2.9	55.5	3.5	20.3	1.5
V	7.2	1.8	7.5	1.8	12.2	1.5
Mn	2.6	1.6	2.4	1.6	3.5	1.4
Fe	33.1	1.9	35.6	1.6	40.5	1.4
Ni	4.5	1.7	3.5	1.9	7.0	1.4
Cu	6.6	2.1	6.8	2.5	3.2	1.4
Zn	27.4	2.4	21.3	1.9	29.4	1.6
As	1.1	2.0	1.0	2.0	1.1	2.0
Se	0.7	2.1	0.5	2.0	1.4	1.5
Br	10.6	2.3	16.8	1.8	14.2	1.8
Cd	0.7	2.4	1.2	2.5	0.6	1.9
Pb	46.9	2.2	35.3	2.2	73.2	1.6
N=30			N=61		N=19	

Table 2b Geometric means and standard deviations of mass ($\mu\text{g}/\text{m}^3$) and elemental (ng/m^3) concentrations in Onondaga County.

Element	Non-Smoking		Smoking		Outdoors	
	Mean	σ	Mean	σ	Mean	σ
Mass	14.4	1.7	36.5	2.4	15.8	1.5
Si	117.1	1.8	83.4	2.4	122.5	1.5
S	874.5	1.6	909.5	2.7	1420.5	1.4
Cl	31.0	4.1	117.0	3.4	19.4	1.7
K	64.5	2.2	296.2	3.6	68.7	1.7
Ca	103.1	3.5	98.8	2.3	77.4	1.9
V	2.2	2.2	3.5	1.9	3.3	1.8
Mn	2.9	1.9	3.2	1.5	4.6	1.6
Fe	37.1	1.8	45.8	1.5	53.9	1.6
Ni	1.0	1.8	0.9	1.7	1.4	1.7
Cu	5.6	2.9	5.0	2.6	2.0	1.5
Zn	12.0	1.7	15.1	1.4	18.8	1.5
As	0.7	1.8	0.9	2.1	1.2	1.8
Se	0.5	1.9	0.4	2.1	1.4	1.7
Br	4.0	1.7	9.4	2.0	8.0	1.8
Cd	0.5	2.9	1.5	2.2	0.6	2.3
Pb	15.2	1.9	17.2	1.7	30.4	1.7
N=45			N=80		N=36	

Table 3 Regression coefficients of kitchen concentrations versus living area concentrations (N=98).

ELEMENT	SLOPE	INTERCEPT	R ²
Mass	.92	6.7	.79
Si	.96	7.6*	.94
S	1.02	30.4*	.95
Cl	.84	38.8	.76
K	1.02	28.0*	.89
Ca	.83	18.8	.98
V	.84	1.3	.74
Mn	.76	0.9	.78
Fe	.84	8.4	.87
Ni	1.01	0.0*	.97
Cu	.87	1.6	.91
Zn	1.14	-1.9	.94
As	0.18*	0.9	.04
Se	.59	-0.3	.38
Br	1.08	-0.6*	.94
Cd	.11*	1.1	.01
Pb	1.09	-2.3	.97

Table 4 Regression coefficients of kitchen concentrations versus living area concentrations for smoking homes (N=50).

ELEMENT	SLOPE	INTERCEPT	R ²
Mass	.97	5.2*	.91
Si	.96	3.8*	.98
S	.98	52.0	.99
Cl	.82	50.5	.85
K	.95	70.0*	.88
Ca	.84	20.4	.99
V	.94	0.5*	.81
Mn	.92	0.3*	.88
Fe	.91	4.1	.96
Ni	1.03	0.0*	.98
Cu	.87	1.0	.96
Zn	1.01	1.0*	.87
As	.13*	1.1	.01
Se	.62	0.2	.47
Br	1.08	-0.3*	.96
Cd	.04*	1.2	.00
Pb	1.06	-1.2*	.98

*not significant at the p=.05 level.

CHROMIUM SAMPLING METHOD

By Frank R. Clay

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The method that I am going to describe today is a method that we have developed for the chromium electroplating industry. It has been called a "screening method"; however, our present plans are to use it for compliance. The method is a simplified version of Method 5 that uses a fixed sampling rate and obtains a proportional sample. It is made from simple and readily available inexpensive components and can be used by plant personnel.

There are over five thousand plating and anodizing facilities in the United States, and many are small, family-owned concerns. Many of these firms are too small to afford conventional testing. A conservative estimate of the cost of three isokinetic sampling runs is from \$3,500 to \$5,000 plus travel expenses. Still there exists a need to quantify chromium emissions from these sources.

The original goal of this project was to develop an inexpensive screening method that was ± 50 percent accurate. This method was to be performed at the plant for around \$500 or less, and the results could be used to determine if a conventional test was needed. However, if the screening results indicated that conventional testing was necessary, additional costs would be incurred by the plater, and the combined costs of screening plus conventional testing would place many platers under a financial hardship. What was really needed was an accurate, simple and inexpensive method that would determine chromium emissions from electroplaters.

The sampling train that we have developed costs less than \$600 to fabricate and about \$350 to perform three sample runs. It samples at a constant rate (about 0.75 dscfm) and the sampling time at each point is varied in order to obtain a proportional sample.

This is a slide of the assembled train as used in the field. Stack gas enters the nozzle and flows to the impingers by way of clear plastic tubing. From the last impinger, the gas flows to a critical orifice that fixes the sample rate. After the orifice, the gas goes to the pump and through the dry gas meter to the atmosphere.

I will now describe the individual components of the train, and we will begin with the nozzle, liner, and sheath. The nozzle and liner are combined into one piece and is simply a 1/4-inch I.D. glass or plastic tube with a 90 degree bend. The nozzle end is tapered, which in the case of the plastic tube was done with a pencil sharpener. The sheath is a piece of 1/2-inch diameter tubing (PVC or copper pipe will work just as well) that is used to keep the glass liner from being broken, or in the case of the plastic tubing, to give rigidity to the apparatus.

From the probe assembly, stack gas flows to the impingers. The train that was used to obtain field samples was assembled using expensive Greenburg-Smith impingers. The impingers, clamps and connecting glassware cost about \$550. In order to reduce costs, this glassware was replaced with the impingers shown in the slide. These are made of Mason jars, plastic or glass tubing, polyester body putty, and silicone rubber cement. The cost of an impinger using the plastic tubing is about \$1.45 for materials while the glass tubing impinger costs \$1 more. It takes about an hour to make each impinger. If labor cost is \$10 per hour, two impingers with plastic tubing would cost \$22.90. It is possible to do the same job with the Mason jar impingers as it is with the Greenburg-Smith impingers, but for \$527 less.

From the impingers, the gas flows through a critical orifice. If a 0.47-atmosphere vacuum is placed on the downstream side of a critical orifice, flow through the orifice will be at the speed of sound and a constant flow rate would be obtained. Knowing this, the initial idea of using the critical orifice was to determine the sample volume without using a dry gas meter. Laboratory work showed that this concept was not practical, but the orifice did work well to control the flow through the train. As a result, the critical orifice is simply a flow control device and sets the sampling rate at about 0.75 dscfm which is the same sampling rate as our standard isokinetic sampling train.

The orifice is made of brass tubing that is available in any hobby shop. A 1/8-inch I.D. piece of tubing 3 inches long is cemented (epoxy) into two larger pieces of brass tubing to make the assembly. Materials cost about \$0.96, and 1/2 hour of labor is required to produce it.

The gas goes from the orifice to a rotary vane pump. The pump is the most expensive component of the train and costs \$233.

The next item in the train is the dry gas meter which is used to determine sample volume. Water displacement and calibrated orifices were also considered for volume determination, but the dry gas meter seems to be the easiest and least error-prone method to use. The cost of a dry gas meter is \$180.

One additional item that was going to be used in this method was an HP-41 CV calculator with a special plug-in module. The module would contain all the programs necessary to perform the testing and to determine emission rates. The calculator/module combination was inexpensive and easy to use. Unfortunately, Hewlett-Packard has discontinued production of the HP-41 calculator, but there are other Hewlett-Packard calculators such as the HP-42S or the HP-48SX that may be suitable. Since many firms have computers, there is also the possibility of writing a computer program that will simplify calculations. While a substitute for the HP-41 has not yet been found, it is not a major problem and rather than specify a single approach to performing calculations, several options will be offered instead.

The procedure for taking a sample is pretty simple and should be relatively easy for the plating facility to perform. This will be facilitated by a video tape that we are planning to produce.

To perform a test, a site is located and ports are installed as specified in Reference Method 1 in Part 60 of the Code of Federal Regulations. Twenty-four sampling points are located, and a velocity traverse is performed using Method 2 of Part 60. These data are used to determine the specific sampling time for each point ((point velocity ÷ average velocity) x base

time). When this has been done, all the operator has to do to obtain a sample is to turn on the pump, place the probe at the appropriate point, and sample for the specified number of minutes and seconds required at that point. This procedure is repeated until all points have been sampled.

When the sampling has been completed, the sample is recovered by rinsing the probe and connecting tubing into the first impinger jar. A piece of plastic wrap is placed over the mouth of the jar, and a standard Mason jar lid and band are used to seal the sample. The impinger jar now becomes the sample jar which can be sent to a laboratory for analysis. The laboratory will analyze the sample for hexavalent chromium using the diphenylcarbazide colorimetric method. The estimated cost for the analysis is \$50.00 per sample or \$150.00 for three sample runs.

Once the laboratory has given the chrome plater the total amount of hexavalent chromium, concentration and mass emission rates may be determined.

The reasons that make the method work are also its limitations. It requires ambient temperature, ambient moisture, ambient air, and a small particle size. With ambient temperature, there is no need to heat the probe, and the temperatures encountered will be from 60 to 120 degrees F. Ambient moisture eliminates the need for a Method 4 run, and moisture can be determined from a wet-bulb dry-bulb thermometer or from a relative humidity indicator. The molecular weight of ambient air is always 28.95, so the need for an ORSAT (Method 3) sample is eliminated. Lastly, the particle size of the sample must be less than 10 microns in diameter. The small particles found in chromic acid gas streams act more like a gas than a particle so that isokinetic sampling is not critical.

During field sampling with this method, it was found that locations close to the plating tank did not produce good results. The mist coming off the plating tank bath tends to collect on the duct work close to the tank and then become reentrained in the gas stream. This means that there is a varying particle size distribution in this area and isokinetic sampling is necessary to obtain a more representative sample. As the distance from the plating tank is increased, the larger particles in the gas stream collect on the walls of the duct and are not reentrained; thus, particle size becomes more uniform. The method works after a control device, or far enough downstream from the plating tank that all the particles are 10 microns or less in diameter.

In the future, we plan to produce a video tape showing how to use the method as well as how to fabricate the sampling train. We will also write an instruction booklet that will make calculations as simple as possible.

The initial goal of this project was to produce a screening method that was ± 50 percent accurate and costs \$500 or less to perform. At the present time, we feel that our method is as accurate as our isokinetic method at outlet locations, is suitable for compliance, and costs \$350 to perform.

DEVELOPMENT OF A SOURCE TEST METHOD FOR HEXAVALENT CHROMIUM

by

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Introduction

Chromate is a strong oxidizing agent, and has a wide industrial application as such, in electroplating and as an intermediate in the production of chromium salts from chromium ores. The latter are employed in pigments, tanning and a great variety of other processes. There is concern regarding the nature of the chromium species in the emissions from combustion sources. Hexavalent chromium, Cr(VI), is a known carcinogen, while trivalent chromium, Cr(III), is not so considered. A comprehensive document has been released by EPA on the health assessment of chromium (1). The trivalent oxide is the most stable of the chromium oxides and is formed by heating the metal or Cr(VI) oxide in air (2). However, when fused with alkaline substances, air oxidation of Cr(III) to Cr(VI) may take place (3). On the other hand, hexavalent chromium may react with any reducing agents present and be converted to Cr(III). Thus, because of these competing processes and the importance of determining the risk that chromium emissions present to the public, a study was undertaken to develop a source test method to measure chromium species in emissions from combustion sources.

However, significant problems may result in Cr(VI) sampling and analysis. That species often occurs at relatively low concentrations, but which are nonetheless environmentally significant. Low concentrations require lengthy sampling times to concentrate the sample, but such procedures also concentrate interfering substances that alter the valence states of chromium. Thus, techniques that preserve chromium valence states must be an important feature of chromium speciation methodology. Several studies (4), (5) have been done to develop source test methods for chromium speciation. However, these methods have addressed emission sources from which interfering substances were largely absent. The present study deals with a sampling system that collects chromium emissions in alkaline solution, in which the species are quite stable. The sampling train utilized a recirculating feature that continuously rinsed the sample probe with the collecting reagent. Samples were analyzed for Cr(VI) using an ion chromatograph with a post column reactor that employed the diphenyl carbazide spectrophotometric procedure. Valence stability was assessed using the radio-active isotope, Cr51, in the chromate form.

Experimental

A multiple hearth incinerator using lime and ferric chloride for sludge conditioning and having a high concentration of chromium in the sludge was tested. Multiple, independent sampling trains were employed. A schematic of the recirculatory sampling train is shown in Figure 1. All portions of the train that came in contact with the sample were Teflon or glass. A Teflon aspirator capable of recirculating absorbing reagent at 50

ml/min while operating at 0.75 cfm was employed. A Teflon union-T was connected behind the nozzle to provide the absorbing reagent/sample gas mix. The absorbing solution was 0.2 molar NaOH with additions of hexavalent ^{51}Cr to determine the extent of conversion of Cr(VI) to Cr(III). Sampling was conducted for from 2 - 4 hours, and from 2 - 5 cubic meters of gas were collected. Following sampling, the trains were flushed with nitrogen gas and the samples were recovered and filtered using an all-Teflon system with a 0.45 micron filter. The samples were analyzed for Cr(VI) using a model 2110i Dionex Ion Chromatograph equipped with a post column reactor that employed the diphenyl carbazide process and a UV/Vis detector. Conversion of Cr(VI) was determined by measuring the ^{51}Cr eluted with the Cr(VI) peak.

Results

The results of measurements made at a sewage sludge incinerator are shown in Table 1. Two problems were encountered: the reduction of Cr(VI) by sulfur dioxide, and the slow oxidation of Cr(III) in the alkaline collection medium. A 30-minute nitrogen purge of the train at 20 liters/minute followed by pressure filtration eliminated these problems. Conversion was almost completely eliminated, as shown in Table 2.

Ratios of CO/CO_2 were also measured at the incinerator and are plotted vs. the Cr(VI)/Cr(III) ratios in Figure 2. A relationship between good combustion and higher Cr(VI) is evident. At low CO levels (good combustion) the ratio of Cr(VI) to Cr(III) is highest, with approximately 10% of the total chromium in the hexavalent form. At high CO levels (poor combustion), the hexavalent chromium is significantly reduced.

Mechanism of Chromate Reduction

The procedures that improved the stability of the chromate samples, flushing with nitrogen to remove dissolved gases and filtering to remove insoluble Cr(III) hydroxide, suggested the importance of obtaining some information about the interfering processes. In sampling combustion sources, the most important of these is the reduction of chromate by sulfur dioxide. Although reduction to the trivalent chromic state by sulfur dioxide in acid solution is the usual method for the treatment of chromate-containing waste waters, this reaction has received little attention. Only one kinetic study has been reported (7), which was carried out in acid solutions, and at relatively high concentrations where dichromate was the predominant species.

The present study was carried out in alkaline solutions and at low concentrations where the chromate ion predominated. Solutions were prepared containing chromate in the parts-per-billion range and sodium sulfite at higher concentrations (~.02M) which approximated the values produced by sampling a gas stream containing 100 ppm SO₂. The pH was set using sulfuric acid and the ionic strength was held constant at 0.2M by addition of sodium sulfate. This ionic strength value was selected because it was the value of the collecting solution in the recirculating sampling train. The pH of the reaction mixtures was measured with a Model 701A Orion Research pH meter; it remained relatively unchanged during the course of the kinetic reactions.

Because the sulfite ion concentration greatly exceeded the chromate concentration, pseudo-first order kinetics were observed. However, the reaction rate was shown to be

proportional to both reactants:

$$\frac{d[\text{CrO}_4^{=}] }{dt} = k[\text{CrO}_4^{=}][\text{SO}_2^*]$$

In this equation, the unionized S(IV) species is assumed to be the reactant, because of the low probability of reaction between similarly charged ions, and because the pseudo-first order rate constant varies with pH approximately as does $[\text{SO}_2^*]$. (The designation SO_2^* indicates the combined sulfur dioxide and sulfurous acid concentrations.) These concentrations were calculated using the concentrations of added sulfite, the pHs, published values of the acid dissociation constants (8), and standard acid-base equations.

Calculation of second-order rate constants (Table 3) indicated that the reaction was controlled by a general acid catalysis, and multiple regression analysis was performed to determine the contributions by hydronium ion and bisulfite ion to the reaction rate. The results (Table 4) indicated that both species produced significant contributions. Evidence for general acid catalysis received further support when reactions were run in phosphate buffer. Under those conditions, the reaction rate increased markedly (Table 5). The contribution of phosphate to the rate constant was determined by estimating the hydronium and bisulfite ion contributions, and subtracting those values from the measured rate constants. Further evidence that unionized S(IV) species were the principal reactants was provided by the phosphate buffer studies, where the effects of hydronium and bisulfite ions were swamped out. Plots of the log of the pseudo-first-order rate constants vs. pH yielded a slope very

close to 2 (Figure 4), indicating that the rate constant varied in the same manner that $[\text{SO}_2^*]$ varies in the pH range of the investigation.

The presence of acid catalysis provides additional information about the chromate-sulfur dioxide reaction. Cr(VI) is known to transfer its electrons in a series of steps, in which the conversion from the Cr(V) valence state to Cr(IV) is rate determining, because a change in coordination number from 4 to 6 occurs (9). General acid catalysis indicates that the transfer of a hydrogen ion facilitates this changeover in the chromate-sulfur dioxide reactive intermediate.

These mechanistic studies also have practical significance, and indicate the importance of collecting Cr(VI) at pH's above 8 and avoiding the use of buffers that catalyze the reaction with sulfur dioxide.

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TABLE 1

SAMPLING RESULTS FOR HEXAVALENT CHROMIUM EMISSIONS
FROM A SEWAGE SLUDGE INCINERATOR

Run No.	Conversion of hexavalent chromium during sampling	Cr(VI) micrograms/dscm	Relative error
3	1.2	0.15	
	1.1	0.06	
	24.6	0.03	
	12.7	0.01	-
7	18.1	0.17	
	12.6	0.15	
	15.3	0.16	
	9.6	0.14	21%
9	6.1	0.18	
	3.3	0.29	33%
11	5.4	0.31	
	2.7	0.38	14%
13	6.0	0.04	
	3.2	0.02	47%

TABLE 2

STABILITY STUDY OF SEWAGE SLUDGE
INCINERATOR EMISSION SAMPLESHexavalent Chromium Concentration, ppb

<u>Run No.</u>	<u>10/25/89</u>	<u>12/12/89</u>	<u>difference</u>
9	0.78	0.80	0.02
	0.46	0.46	0.00
11	0.57	0.59	0.02
	0.52	0.57	0.05
13	0.25	0.29	0.04

TABLE 3

VARIATION OF RATE CONSTANT WITH HYDROGEN ION AND BISULFITE ION CONCENTRATIONS

$k, \text{ L/M}\cdot\text{hrs}^{-1}\cdot 10^{-6}$	$[\text{H}^+], \text{ M/L}\cdot 10^7$	$[\text{HSO}_3^-], \text{ M/L}$
2.68	0.43	0.0078
6.78	1.02	0.0120
7.78	1.01	0.0240
2.75	0.28	0.0205
0.67	0.16	0.0132
6.45	0.49	0.0295

TABLE 4

DEPENDENCE OF RATE CONSTANT
ON HYDROGEN ION AND
BISULFITE ION CONCENTRATIONS

$$k = k_0 + k_1[H^+] + k_2[HSO_3^-]$$

	Rate Constant	Std. Dev.
k_0	-8016	4812
k_1	5.60E13	1.22E13
k_2	8.66E7	4.15E7

TABLE 5
EFFECT OF THE PRESENCE OF PHOSPHATE BUFFER
ON THE CHROMATE-SULFUR DIOXIDE REACTION RATE

pH	k, L/M*hrs ⁻¹ *10 ⁻⁷			[H ₂ PO ₄ ⁻]	k ₃ *10 ⁻⁸
	k _p	k _s	k _p -k _s		
7.030	2.71	0.72	1.99	0.0238	8.34
7.311	1.26	0.40	0.86	0.0139	6.20
7.330	2.22	0.39	1.83	0.0256	7.16
7.460	0.89	0.30	0.59	0.0124	4.74
7.746	1.75	0.18	1.58	0.0275	5.74
7.921	1.64	0.13	1.51	0.0280	5.41
				mean	6.27
				std. dev	1.2

k_p: measured rate constant with phosphate buffer present.

k_s: calculated rate constant with only bisulfite present.

k₃: general acid catalysis contribution by phosphate,

$$k = k_0 + k_1[H^+] + k_2[HSO_3^-] + k_3[H_2PO_4^-]$$

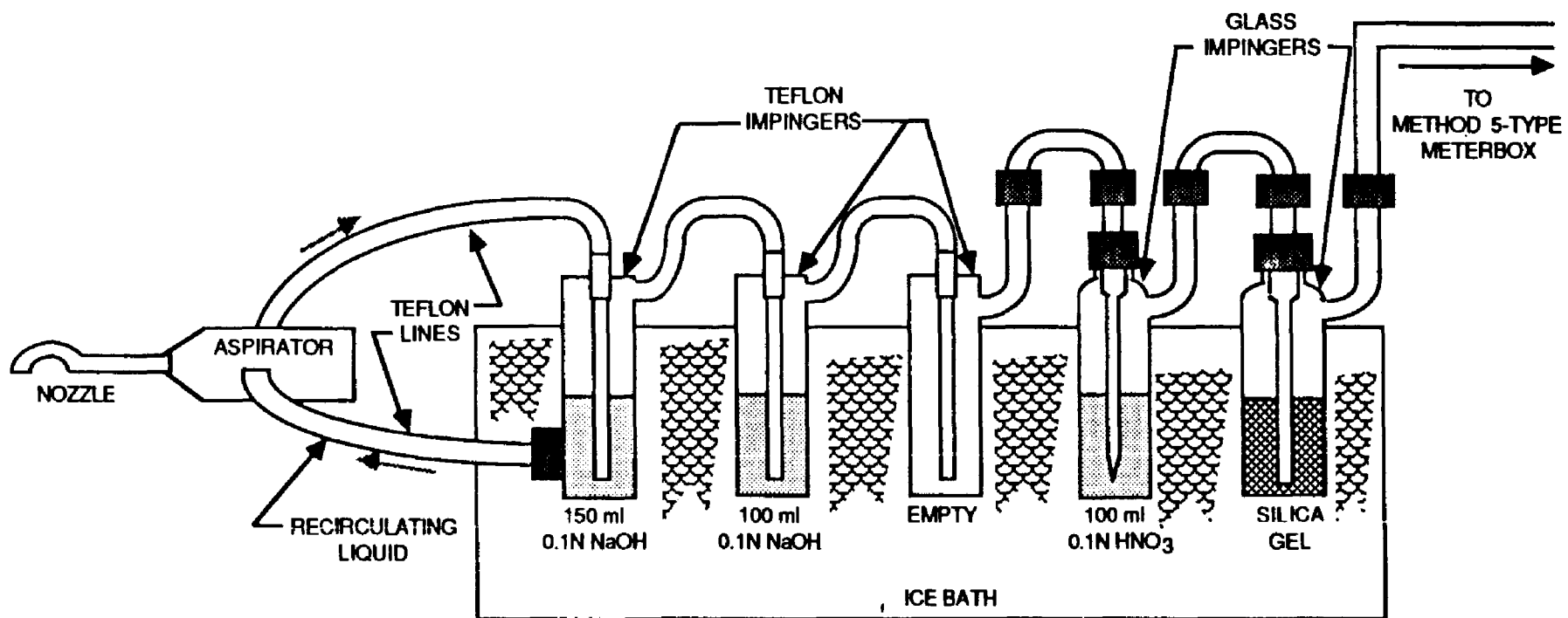
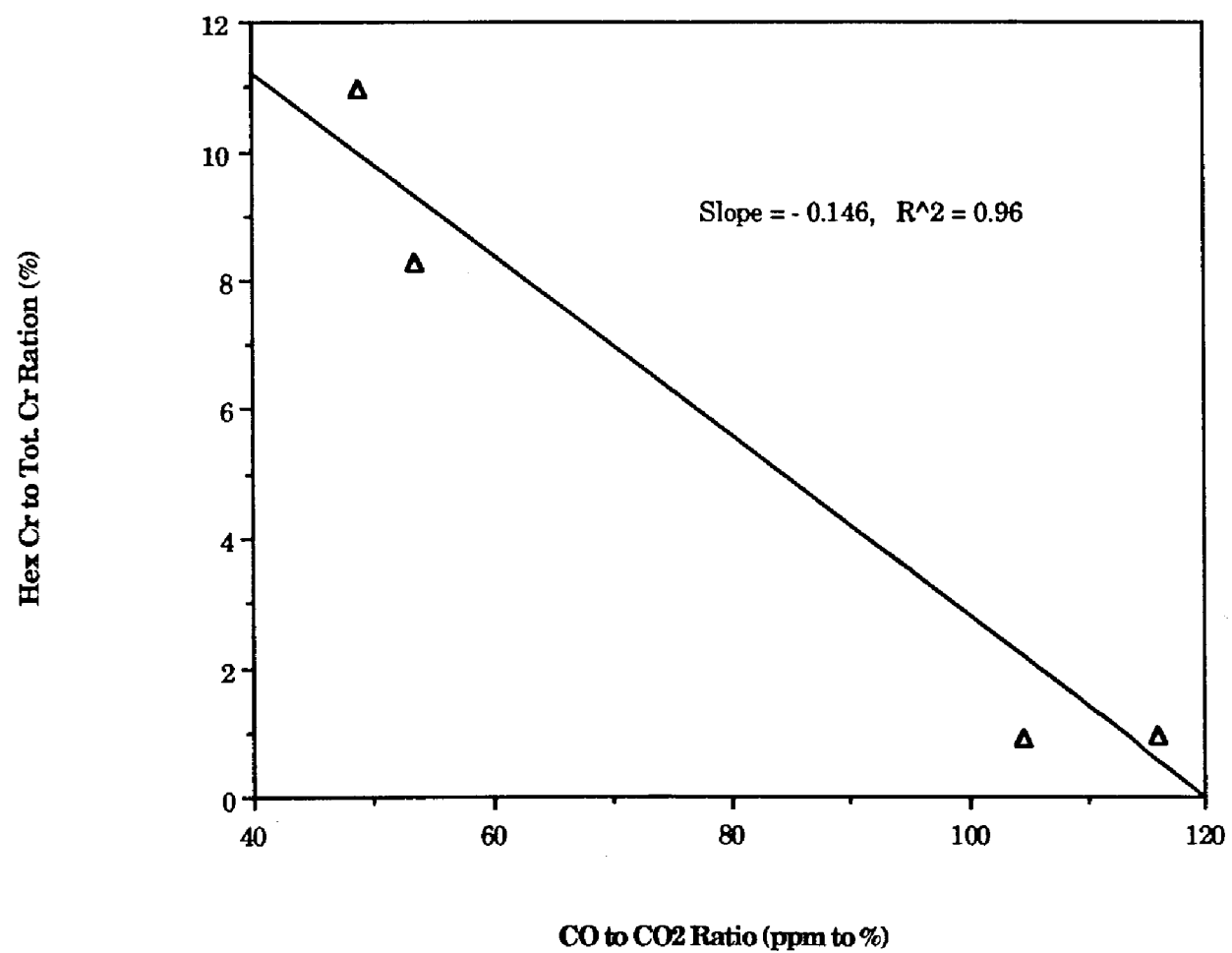
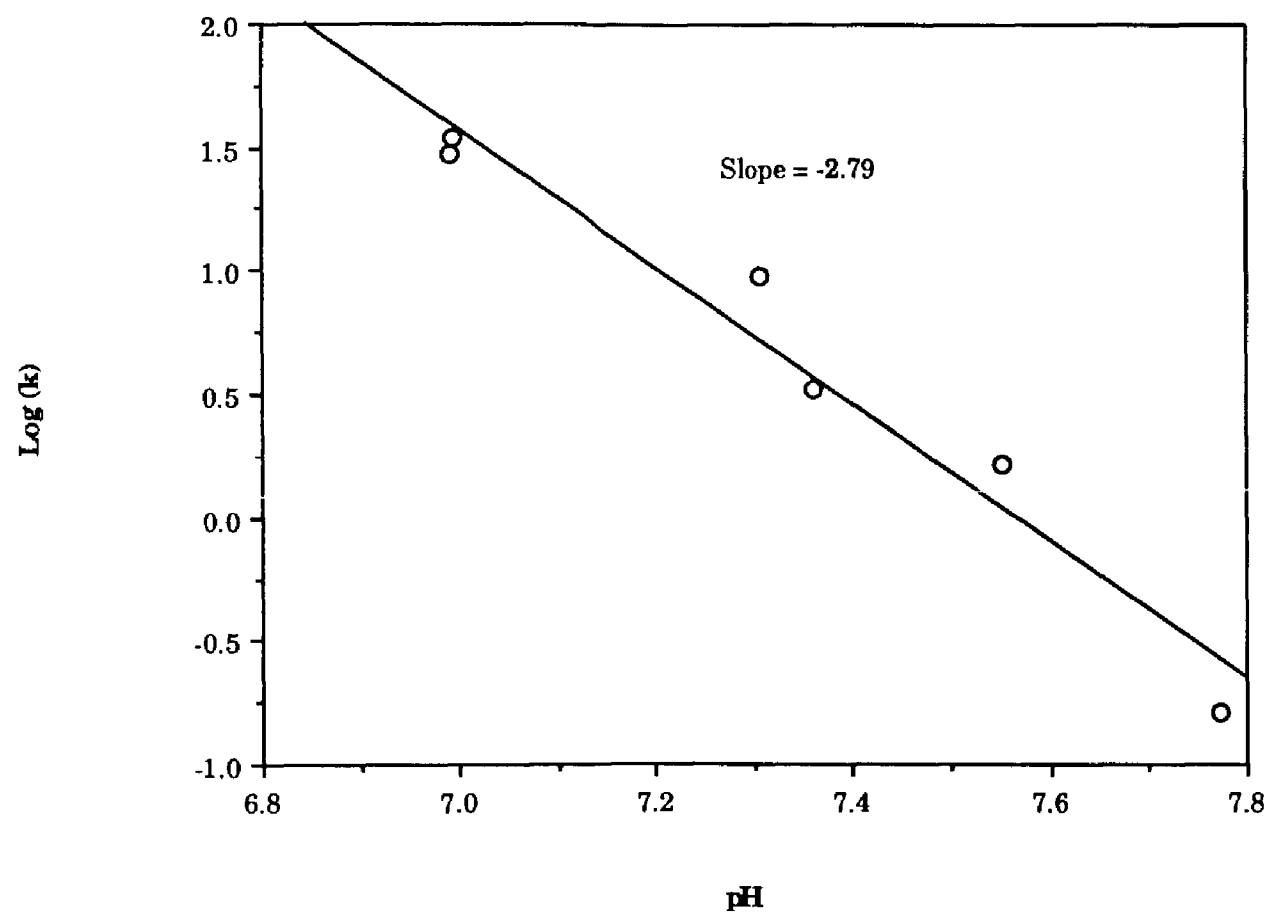


Figure Cr^{+6} -1. Schematic of recirculatory impinger train.

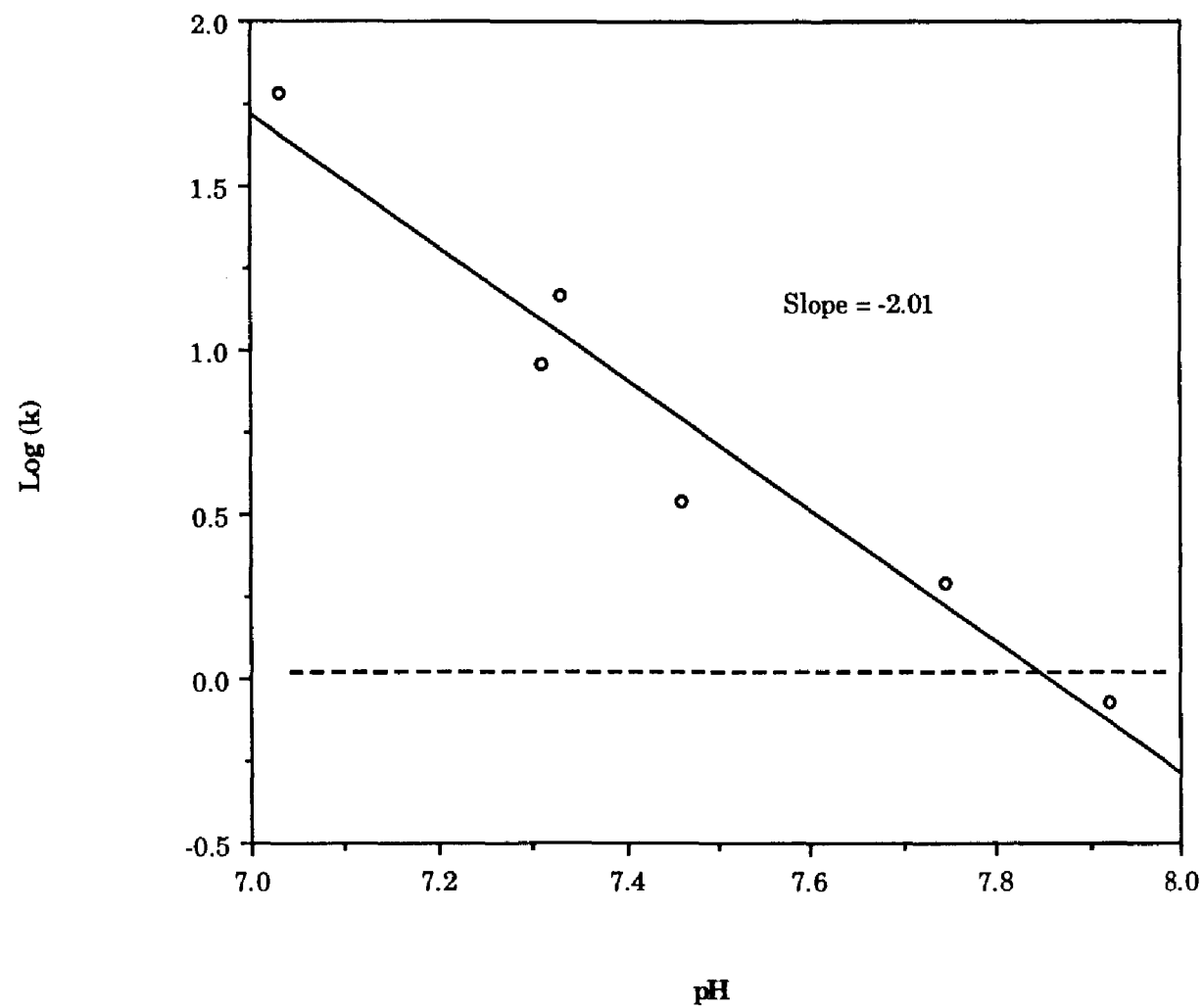
Hex Cr/Total Cr vs CO/CO2 Ratios



Log of Psuedo-First Order Rate Constant vs pH



Log (k) vs pH in Phosphate Buffer



DEVELOPMENT AND FIELD VALIDATION OF A SAMPLING AND
ANALYTICAL METHOD FOR AIRBORNE HEXAVALENT CHROMIUM

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Hexavalent chromium [Cr(VI)] is classified as a human respiratory carcinogen by the U.S. Environmental Protection Agency (USEPA). Airborne Cr(VI) emissions are associated with a number of industrial sources including metal plating, tanning, chromite ore processing and spray painting operations; combustion sources such as automobiles and incinerators; and fugitive dusts from contaminated soil. To date, only a workplace sampling and analytical method has been developed and validated for measuring airborne Cr(VI). The method can detect concentrations as low as $0.5 \mu\text{g}/\text{m}^3$; however, environmental concentrations of airborne Cr(VI) are about 1000-fold lower than this limit of detection. No sampling and analytical method specific to Cr(VI) at environmental concentrations has been previously field tested. This paper describes a sampling and analytical method for the quantitation of airborne Cr(VI) at concentrations as low as $0.1 \text{ ng}/\text{m}^3$. The collection method uses three 500-ml glass impingers in series, each fitted with Greenberg-Smith impactors operated at 15 liters per minute (lpm) for 24 hours, and containing sodium bicarbonate buffer solution. The average collection efficiency in the first two of three impingers was 81% of the mass for airborne Cr(VI) particulate concentrations of 3 to $10 \text{ ng}/\text{m}^3$. It was found that both Cr(VI) and Cr(III) were stable in the collection medium. The described method was used to measure ambient levels of hexavalent chromium at sites having chromium-contaminated soil.

Introduction

Airborne hexavalent chromium [Cr(VI)] emissions are associated with a number of industrial operations. The focus of this study is a Cr(VI) source of more recent concern, the release of fugitive dusts from contaminated soil. Although chromium may exist in several valence states, trivalent chromium [Cr(III)] and Cr(VI) are the two valences of interest for human health. Cr(III), which is relatively non-toxic, is the predominant naturally occurring environmental form of chromium, and an essential human dietary mineral. In contrast, Cr(VI) is primarily man-made and has been shown to be carcinogenic to humans exposed to relatively high levels in the workplace air. Therefore, the differentiation between airborne concentrations of Cr(VI) and Cr(III) is important in the assessment of potential human hazards from chromium.

At present there is no standardized method with the necessary specificity and sensitivity for measuring environmental levels of airborne Cr(VI), particularly from contaminated soil. The NIOSH Method 7600, developed in 1984, has been used to measure Cr(VI) concentrations in the occupational setting. This method uses a 37-mm diameter, 5.0 μ m pore size PVC membrane filter for collection, and Visible Absorption Spectrophotometry (VAS) for quantitation of Cr(VI). However, the detection limit of the NIOSH method is 500 ng/m³⁽¹⁾, approximately 25 to 50 times higher than typical environmental concentrations of airborne total chromium^(2,3). Refinements of Method 7600 for environmental sampling applications have achieved some increase in analytic sensitivity, although, in some cases, at the cost of specificity for Cr(VI)^(4, 5, 6, 7, 8, 9). The increased sensitivity that these refinements produce still does not meet the needs of environmental sampling.

In 1987, the California Air Resources Board (CARB) developed a sensitive sampling and analytical procedure to measure Cr(VI) downwind of industrial point sources⁽¹⁰⁾. The CARB method, which relies on the water solubility of airborne chromium-containing particulates for collection, is a modification of EPA Method 5 that was originally proposed by the Research Triangle Institute⁽¹¹⁾. This method is currently being evaluated by California's South Coast Air Quality Management District (SCAQMD)⁽¹²⁾. A typical impinger train consists of three Greenberg-Smith impingers in series. The first and second impingers are filled with 100 ml of a 0.02 M sodium bicarbonate solution (pH 8-9), and the third impinger is empty. The buffer solution prevents the reduction of Cr(VI) also ensuring stability during preparation and analysis. The CARB method makes use of an ion chromatography (IC) column to separate the Cr(VI) from the impinger solution for quantitation. Following chromatographic separation, the Cr(VI) is complexed with diphenylcarbazide and measured spectrophotometrically at 520 nm. The limit-of-detection (LOD) of the CARB method for a 20 m³ air sample is approximately 1 to 0.1 ng/m³ depending on whether a preconcentration step is used in sample preparation.

After reviewing the available methods, it was concluded that the CARB method offered the specificity and stability, as well as the analytical sensitivity, required to assess environmental concentrations of airborne hexavalent chromium. Although the CARB method has been used for regulatory compliance, field validation of the method has not been conducted. Further, the applicability of the method to the sampling of airborne soil particles containing Cr(VI) has not been demonstrated⁽¹¹⁾. This paper describes the development and field validation of an impinger/IC method that can accurately quantitate the airborne concentration of Cr(VI) over a fairly

wide range (0.5 to 50 ng/m³). The field study was restricted to validating the method at sites of Cr(VI) contaminated soil, although this method should be applicable to Cr(VI) in a mist or fume.

Experimental Materials and Methods

The Cr(VI) sampling train consisted of three glass 500-ml impingers in series filled with 0.02 M sodium bicarbonate solution followed by a 37 mm diameter, 0.5 μ m glass-fiber backup filter. The impinger series was placed in an ice bath. The impinger train was connected to a Dwyer pump, and was calibrated using a Gilman digital flow meter. A Gilmont compact rotameter was placed in-line between the cassette and the pump for the purpose of identifying any changes in the flow rate.

Air was drawn through the sampling train at a rate of approximately 15 liters per minute. Flow rate calibration was performed at the beginning and at the end of the 24-hour sampling period. Sampling apparatus parameters were monitored every 4-6 hours. The impinger solution volume and pH were recorded at the beginning and end of the sampling period. All samples were transported on ice to the analytical laboratory within 24 hours after collection. Strict adherence to a decontamination protocol was necessary to prevent soil contamination of the sampling equipment. Prior to sampling apparatus assembly, impingers and tubing were soaked in a dilute nitric acid (1%) bath, rinsed three times with distilled water, and "charged" once with buffer solution. Field blanks were included for every sampling period.

This collection method differs from that used by CARB in two ways: 1) the volume of buffer in each impinger is 200 ml, rather than 100 ml, and 2) the third impinger contains fluid rather than being empty. These modifications were made to enhance the particulate Cr(VI) collection efficiency of the sampling train by providing an additional impaction step (the 3rd impinger) and an increased contact time (additional impinger solution).

Cr(VI) collected in the buffer solution was separated using IC. The IC column was packed with IonPac AS7 (manufactured by Dionex). The eluent consisted of 0.25M ammonium sulfate and 0.1M ammonium hydroxide at a pH of 7.0. The eluent was passed through the column at a flow rate of 1.5 ml/min. The chromate ion eluted at 3.5 to 4.0 minutes and was then complexed with 0.002 M diphenylcarbazide. The red chromium complex was spectrophotometrically quantified at 520 nm. Based on a total sample volume of 20 m³, the approximate LOD of Cr(VI) in air for this method is 0.1 ng/m³.

Study Design and Results

Breakthrough

The breakthrough of Cr(VI) in solution, i.e., breakthrough from one impinger to the next, was assessed by drawing air through four different sampling trains at 15 lpm for a 24 hour period. Trains 1 and 2 contained two impingers in series with the first impinger spiked with 10 ng/L Cr(VI). Trains 3 and 4 contained unspiked buffer. A 37 mm diameter, 0.5 μ m pore size TeflonTM filter was placed ahead of the impingers in all the sampling trains to prevent the collection of any chromium contaminated particulates. Trains 1 and 2 were used to assess the potential movement of Cr(VI) in solution from the first to the second impinger. Trains 3 and 4 were used

to demonstrate that detectable levels of ambient chromium were not collected by the sampling trains during these tests.

No detectable amount of Cr(VI) was transported from the first impinger to the second and no ambient chromium was collected.

Collection Efficiency

The impinger collection mechanisms for chromium contaminated particulates likely involve a combination of impaction and solubility. The sampling flow rate is a key variable influencing particle collection efficiency for both of these collection mechanisms. In evaluating the effect of flow rate, collection efficiency is defined as the percentage of the total amount of Cr(VI) collected by the sampling train that was found in the first impinger. No statistically significant difference in the concentration of Cr(VI) in the first impinger was found for flow rates of 5, 10, and 15 L/min. Samples where the total Cr(VI) concentration was at least ten times the limit of detection, most of the chromium was collected in the first two impingers in series. In approximately 73% of these sampling trains less than 15% of the total Cr(VI) mass was in the third impinger indicating good relative collection efficiency at environmental relevant Cr(VI) concentrations.

Cr(VI) Stability

To assess the stability of Cr(VI) in the buffer solution, a 10 µg/L field spike sample was analyzed on days 2, 6, 8, 10, 13, 15, and 20 after spiking. The Cr(VI) concentrations were not significantly different over the twenty day storage period, indicating that samples are stable and do not require immediate analysis following collection.

Cr(III) Stability

Under environmental conditions, Cr(III) is expected to make up a large portion of total airborne chromium. The oxidation of Cr(III) to Cr(VI) is therefore a potential concern to be addressed in sampling for Cr(VI). Under reduced temperature conditions approximately 0.2% of a 1000 µg/L Cr(III) spike was converted to Cr(VI). The portion converted under ambient temperature conditions was 0.7%. Based on the results of a t-test, there was no statistically significant difference between the groups at the 95% confidence limit. This conversion is not expected to have a measurable effect on Cr(VI) concentrations at the concentrations of total airborne chromium typically sampled in ambient urban air since they are 10 to 100 times less than the Cr(III) spike level used in this experiment.

Precision and Spike Recovery

TriPLICATE co-located impinger sampling trains, designated 1, 2, and 3, were used to assess the combined sampling and analytic precision. As presented in Table I, the pooled coefficient of variation between replicates was 20%. These data indicate that the method precision is within the range specified by the USEPA - Contract Laboratory Program for quantification of trace metals⁽¹³⁾. This level of precision is also well within the range expected for industrial hygiene sampling procedures⁽¹⁴⁾.

True accuracy of the sampling and analytical methods could not be determined since a Cr(VI) reference standard was not available. As a surrogate measure, analytic accuracy was assessed as a function of recovery

of a 1 $\mu\text{g/L}$ Cr(VI) field spike in the validation study program. Additionally, 10 $\mu\text{g/L}$ Cr(VI) field spikes were collected throughout the sampling program. As presented in Table II, under both reduced (ice bath) and ambient temperature conditions, spike recovery of the 1 $\mu\text{g/L}$ Cr(VI) spikes ranged from 87 to 99%. The mean percent recovery was approximately 92%. Recovery of the 10 $\mu\text{g/L}$ Cr(VI) spikes analyzed during development of the sampling method ranged from 65% to 118%, with a mean percent recovery of 98%. Based on this data, method accuracy for the validated sampling program is within USEPA-CLP accuracy criteria ($\pm 25\%$) and NIOSH accuracy criteria (i.e., greater than 90%)⁽¹⁴⁾. Additionally, there was no statistically significant difference between the two groups at the 95% confidence limit. These results suggest that Cr(VI) at environmentally relevant concentrations is stable in the buffer solution under both reduced (ice bath) and ambient temperature conditions.

Field Experience

Three hundred samples were collected between August and October 1989 at 17 different Northern New Jersey locations known to have fill material containing chromium residue. The sampling period is believed to represent the time of year during which the potential for dust generation is the greatest. Sampling for total chromium and Cr(VI) was performed at each sampling location. Fourteen of the seventeen sites had indoor locations. At most sites, two outdoor locations, one upwind and one downwind, and two indoor locations were sampled. A summary of the air sampling data is presented in Table III.

Conclusions

The sampling and analytical methods evaluated in this study are sufficiently sensitive and specific for field sampling of airborne hexavalent chromium particulates. Recovery rates are excellent regardless of whether or not an ice bath is utilized during sampling. The combined sampling and analytical method meets the requirements for both spike recovery and precision as specified by EPA criteria. The results of this method development and field validation indicate that the selected sampling and analytical methods fulfill the need for accurate quantitation of ambient concentrations of Cr(VI) in air.

0402ALR1

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TABLE I: METHOD PRECISION

Study	# Replicates	Coefficient of Variation (CV)
1	3	7.4%
2	3	6.8%
3	3	8.9%
4	3	<u>20.0%</u>
Pool CV		10.8%

TABLE II: RECOVERY OF FIELD SPIKES

1 ppb		10 ppb	
Study	% Recovery	Study	% Recovery
1	91%	1	103%
2	87%	2	118%
3	99%	3	90%
		4	95%
		5	117%
		6	97%
$\bar{X}_1 =$	92%	$\bar{X}_2 =$	103%
$S_1 =$	6%	$S_2 =$	12%

TABLE III: AIR SAMPLING DATA SUMMARY

Site Number	Average Indoor $C_p(VI)$ ng/m ³	Average Outdoor $C_p(VI)$ ng/m ³
1	3.2	7.9
2	No building on site	1.1
3	9.6	4.4
4	5.2	7.8
5	No building on site	6.5
6	6.0	9.6
7	3.3	6.9
8	1.5	6.9
9	2.4	6.9
10	1.8	4.3
11	0.2	2.3
12	3.5	2.7
13	3.3	0.5
14	2.3	1.7
15	1.7	3.0
16	1.4	3.3
17	No building on site	2.1
Summary Statistics		
Mean (standard deviation)	3.2 (2.4)	4.6 (2.8)
Geometric Mean (GSD)	2.2 (2.7)	3.1 (3)

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Determination of Average Ambient PCDDs/PCDFs Concentrations in the Vicinity of Pre-Operational Resource Recovery Facilities in Connecticut

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ABSTRACT

Recent regulatory statutes issued by the State of Connecticut require that ambient monitoring for 2,3,7,8-substituted PCDDs/PCDFs be conducted on both a pre-operational and post-operational basis. In response to this requisite, pre-operational monitoring programs designed to determine background levels of PCDDs/PCDFs in ambient air have been completed in the vicinity of four resource recovery facilities located in Bridgeport, Bristol, Hartford and Wallingford, Connecticut. Sampling and analytical methodology involved the use of high volume sorbent samplers in conjunction with high resolution (magnetic sector) mass spectrometry to determine background ambient PCDDs/PCDFs concentrations in the 0.01-0.1 pg/m³ range.

This paper presents average ambient PCDDs/PCDFs levels determined for each of the four pre-operational monitoring networks listed above. Congener profiles established on a region-specific basis will be compared to identify variation in average ambient PCDDs/PCDFs burdens found to occur among the four study areas. In addition, similarities between ambient and combustion source profiles will be examined as will the noted predominance, on a region-specific basis, of certain 2,3,7,8-substituted PCDDs/PCDFs species. Toxicity assessments for each of the four regions will also be presented and compared through application of the EPA Toxic Equivalency Factor (TEF) model to the Connecticut ambient PCDDs/PCDFs database.

INTRODUCTION

The State of Connecticut requires that ambient monitoring for PCDDs/PCDFs be conducted in the vicinity of resource recovery facilities constructed in Connecticut on both a pre-operational and post-operational basis [1]. ENSR Consulting and Engineering has completed such pre-operational studies around four resource recovery facilities located in Bristol, Hartford, Bridgeport and Wallingford, CT. The Hartford and Bristol programs were conducted concurrently from July through September, 1987; the Bridgeport program was conducted from November 1987 to January 1988, and the Wallingford program was conducted from August to October, 1988.

This paper presents average ambient PCDDs/PCDFs levels as determined from conduct of the aforementioned programs. Average ambient PCDDs/PCDFs burdens for the four study regions are presented and compared along with profiles for the tetra through octa PCDDs/PCDFs congener classes and individual 2,3,7,8-substituted PCDDs/PCDFs. In addition, the Connecticut PCDDs/PCDFs average ambient database is applied to the EPA Toxic Equivalency Factor (TEF) model to provide average atmospheric PCDDs/PCDFs burdens expressed as 2,3,7,8-TCDD toxic equivalents on a network-specific basis. These values are then compared to the Connecticut ambient PCDDs/PCDFs standard of 1.0 pg/m³.

SAMPLING AND ANALYSIS METHODOLOGY

General Metal Works Polyurethane Foam (PUF) PS-1 samplers were used to collect the PCDDs/PCDFs isomers listed in Table 1. The samplers are essentially modified high volume air samplers employing a glass fiber filter in tandem with a sorbent trap to collect particulate-associated and vapor-phase PCDDs/PCDFs, respectively. Air flow rates between 140 and 220 lpm were utilized, in conjunction with 24 to 96 hour sample sessions to produce sample volumes between 350 m³ and 950 m³. All PS-1 samplers were calibrated prior to and at the conclusion of each sampling session using an NBS traceable calibrated orifice. Quality Assurance/Quality Control elements implemented for these programs included field blanks, method blanks, field surrogates, internal standards and collocated samples [2].

All program samples selected for analysis were prepared and analyzed based on the protocol outlined in EPA Methods 8280 and 8290. Native dioxins and furans collected from the ambient air were quantified against isotopically labelled internal standards added to each sample prior to extraction with toluene. Extracts were cleaned by column chromatography and subjected to complete PCDDs/PCDFs analyses by high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS). Detection limits of 10 to 50 fg/m³ were achieved.

RESULTS AND DISCUSSION

Ambient air samples were collected as described above in the vicinity of the Bristol (n=23), Hartford (n=31), Bridgeport (n=22), and Wallingford (n=24), Connecticut Resource Recovery Facilities for the target parameters listed in Table 1. An average concentration for each target parameter was calculated for the four study areas listed above, with non-detected values included into the database as one-half the reported detection limit. This treatment of non-detected observations has been discussed by others in the open literature [3,4].

Table 2 provides average ambient concentrations of PCDDs/PCDFs (total Cl₄ through Cl₈) for each monitoring network, which ranged from 1.8 pg/m³ (Bristol) to 7.1 pg/m³ (Bridgeport). These values are comparable to those measured by others from similar ambient monitoring studies [5,6,7]. The PCDDs burden for all networks included a significant contribution from OCDD, which was the predominant species of PCDDs/PCDFs measured at each network during the Connecticut programs.

Seasonal influences and regional transport phenomena may contribute to the variability in average ambient PCDDs/PCDFs burden found to exist among the four monitoring networks. For example, additional combustion source aggregates present during wintertime, may have contributed to the higher PCDDs/PCDFs levels measured at the Bridgeport network. These additional wintertime combustion sources would not have impacted the Mid-Connecticut, Bristol and Wallingford monitoring networks, which were operated during the summer and early fall seasons. It has also been shown that the majority of PCDDs/PCDFs are particulate-associated, particularly at lower ambient temperatures, such as encountered during wintertime [8,9]. For this reason, regional and/or long-range transport of combustion source particulate-associated PCDDs/PCDFs may also contribute to the seasonal variability of PCDDs/PCDFs levels by region. This is particularly likely for the Bridgeport network which may have been impacted by particulate-associated PCDDs/PCDFs originating from combustion sources located in the Metropolitan New York City area [9].

Figures 1 and 2 show the average ambient concentration of the Cl₄ through Cl₈ PCDDs and PCDFs congener classes, respectively, for each of the four monitoring networks. These congener profiles resemble those seen for combustion sources, characterized by higher atmospheric levels of PCDDs as chlorination increases (TCDD < PeCDD < HxCDD < HpCDD < OCDD) [10,11]. The average TCDF and PeCDF levels are higher than the average TCDD and PeCDD levels, while the average HpCDF and OCDF levels are lower than the average HpCDD and OCDD for all four monitoring networks.

Figures 3 and 4 (note fg/m³ concentration scale in these figures) show individual 2,3,7,8-substituted PCDDs and PCDFs, respectively, for the four monitoring networks. As with the PCDD congener class totals, higher average ambient levels are seen with increasing PCDD chlorine substitution for the 2,3,7,8-substituted PCDDs. This phenomena is true for all four study areas. Unlike the 2,3,7,8-substituted PCDDs, there is no trend relating chlorine substitution to average ambient concentration for the 2,3,7,8-substituted PCDFs. Of note,

however, is the predominance of the 1,2,3,4,6,7,8-HpCDF congener in all four monitoring networks.

Ambient PCDDs/PCDFs data gathered from these programs are presented in terms of 2,3,7,8-TCDD toxic equivalents. This is accomplished by applying the EPA Toxic Equivalency Factor model [12], contained in Table 3, to the ambient PCDDs/PCDFs database established through this study. Average toxic equivalents resulting from the EPA TEF model for each of the four ambient monitoring programs are contained in Table 4. The State of Connecticut has issued a standard for ambient PCDDs/PCDFs levels of 1.0 pg/m³ expressed as EPA 2,3,7,8-TCDD toxic equivalents [1]. As noted in Table 4, none of the four regions studied resulted in a toxic equivalents sum which exceeded this standard. The average ambient PCDDs/PCDFs levels expressed as EPA toxic equivalents ranged from 0.012 pg/m³ (Bristol) to 0.049 pg/m³ (Bridgeport). It should be noted that numerous other Toxic Equivalency Factor models exist (Nordic, Ontario, New York, California, International, etc.), each of which produces varying toxicity assessments upon application to the same PCDDs/PCDFs database [13].

SUMMARY AND CONCLUSIONS

Ambient monitoring for PCDDs/PCDFs in the vicinity of pre-operational recovery facilities in Connecticut showed that average burdens of PCDDs/PCDFs vary by region. This regional variation may be explained by seasonal influences and atmospheric transport phenomena. The ambient congener profiles mirror those of combustion sources as seen by the increased predominance of the higher homolog PCDDs congener classes ($Cl_4 < Cl_5 < Cl_6 < Cl_7 < Cl_8$). Also of note is the predominance of certain 2,3,7,8-substituted PCDDs/PCDFs congeners in all four study areas. Specifically, OCDD, 1,2,3,4,6,7,8-HpCDD, 1,2,3,4,6,7,8-HpCDF, and 1,2,3,4,7,8-HxCDF predominated in all four networks. The predominance of these particular isomers in combustion source emissions has been reported elsewhere [14].

The data collected for these programs were applied to EPA's Toxic Equivalency Factor (TEF) model to determine average toxicity in terms of 2,3,7,8-TCDD toxic equivalents. Application of the EPA TEF model showed that average ambient PCDDs/PCDFs levels expressed as EPA toxic equivalents on a seasonal basis exist significantly below the Connecticut standard of 1.0 pg/m³ (expressed as 2,3,7,8-TCDD equivalents on an annual basis) for all four study regions.

ACKNOWLEDGEMENTS

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Table 1. Target Parameter List.

PCDDs	Key	PCDFs	Key
2,3,7,8 – TCDD	1	2,3,7,8 – TCDF	7
1,2,3,7,8 – PeCDD	2	1,2,3,7,8 – PeCDF	8
1,2,3,4,7,8 – HxCDD	3	2,3,4,7,8 – PeCDF	9
1,2,3,6,7,8 – HxCDD	4	1,2,3,4,7,8 – HxCDF	10
1,2,3,7,8,9 – HxCDD	5	1,2,3,6,7,8 – HxCDF	11
1,2,3,4,6,7,8 – HpCDD	6	2,3,4,6,7,8 – HxCDF	12
OCDD		1,2,3,7,8,9 – HxCDF	13
(Also tetra through hepta		1,2,3,4,6,7,8 – HpCDF	14
PCDDs/PCDFs congener class totals)		1,2,3,4,7,8,9 – HpCDF	15
		OCDF	

Table 2. Average Ambient Levels of PCDDs/PCDFs (tetra through octa) for the Connecticut Study Areas

Monitoring Network Location	Season	Average PCDDs Concentration (pg/m3)	Average PCDFs Concentration (pg/m3)	Total Burden (pg/m3)	Number of Samples (n)
Bristol	Summer	1.2	0.6	1.8	23
Hartford	Summer	2.6	0.8	3.4	31
Bridgeport	Winter	4.4	2.7	7.1	22
Wallingford	Summer/Fall	3.8	1.7	5.5	24

Table 3. EPA Toxic Equivalency Factor (TEF) Model.

PCDDs	Toxic Equivalency Factor	PCDFs	Toxic Equivalency Factor
2,3,7,8 - TCDD	1	2,3,7,8 - TCDF	0.1
OTHER TCDD	0.01	OTHER TCDF	0.001
1,2,3,7,8 - PeCDD	0.5	1,2,3,7,8 - PeCDF	0.1
OTHER PeCDD	0.005	2,3,4,7,8 - PeCDF	0.1
1,2,3,4,7,8 - HxCDD	0.04	OTHER PeCDF	0.001
1,2,3,6,7,8 - HxCDD	0.04	1,2,3,4,7,8 - HxCDF	0.01
1,2,3,7,8,9 - HxCDD	0.04	1,2,3,6,7,8 - HxCDF	0.01
OTHER HxCDD	0.0004	2,3,4,6,7,8 - HxCDF	0.01
1,2,3,4,6,7,8 - HpCDD	0.001	1,2,3,7,8,9 - HxCDF	0.01
OTHER HpCDD	0.00001	OTHER HxCDF	0.0001
OCDD	0	1,2,3,4,6,7,8 - HpCDF	0.001
		1,2,3,4,7,8,9 - HpCDF	0.001
		OTHER HpCDF	0.00001
		OCDF	0

Table 4. Average Toxic Equivalents Using EPA TEF Model for Connecticut Study Regions.

Monitoring Network	Average Toxic Equivalents (EPA) (pg/m3)
Bristol	0.012
Hartford	0.027
Bridgeport	0.049
Wallingford	0.014

*Connecticut ambient PCDDs/PCDFs standard is 1.0 pg/m3 (annualized, EPA Model)
expressed as 2,3,7,8-TCDD equivalents.*

Figure 1
Average Ambient Concentrations of PCDDs
Congener Class Sums (Cl_4 through Cl_8)

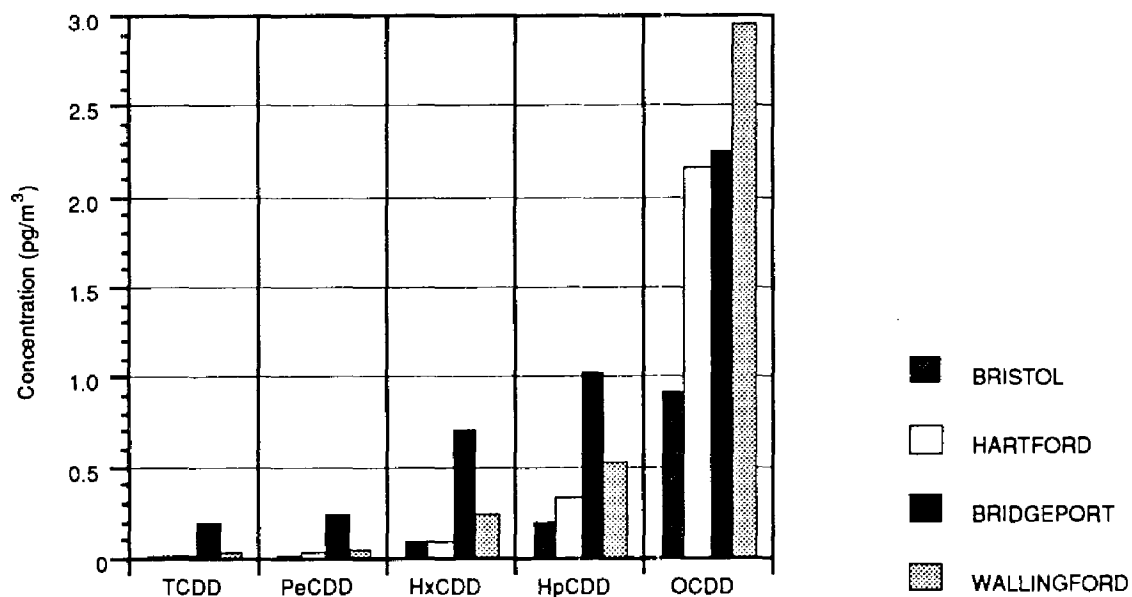


Figure 2
Average Ambient Concentrations of PCDFs
Congener Class Sums (Cl_4 through Cl_8)

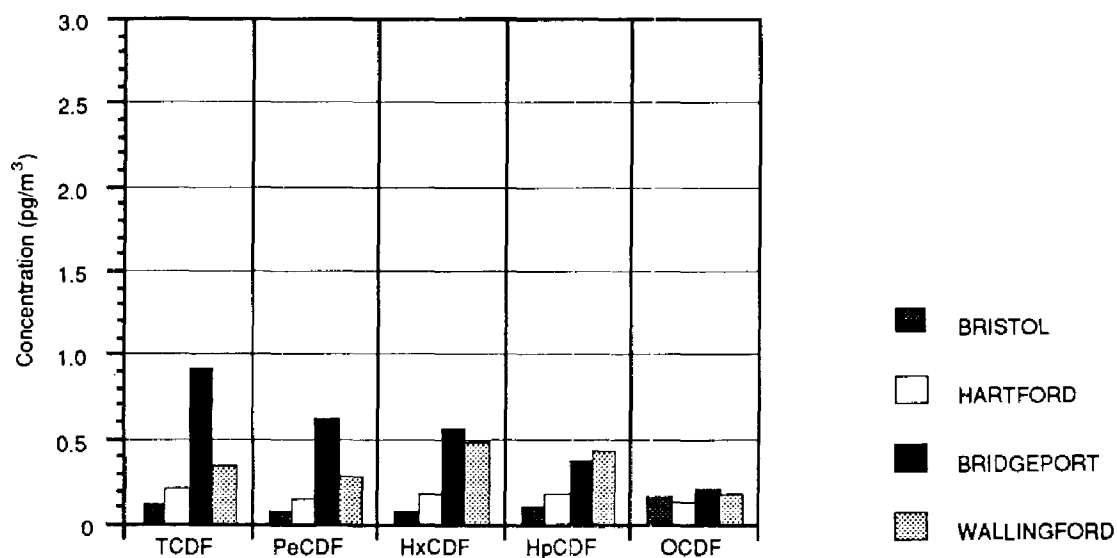


Figure 3
Average Ambient Concentrations of
2,3,7,8 - Substituted PCDDs

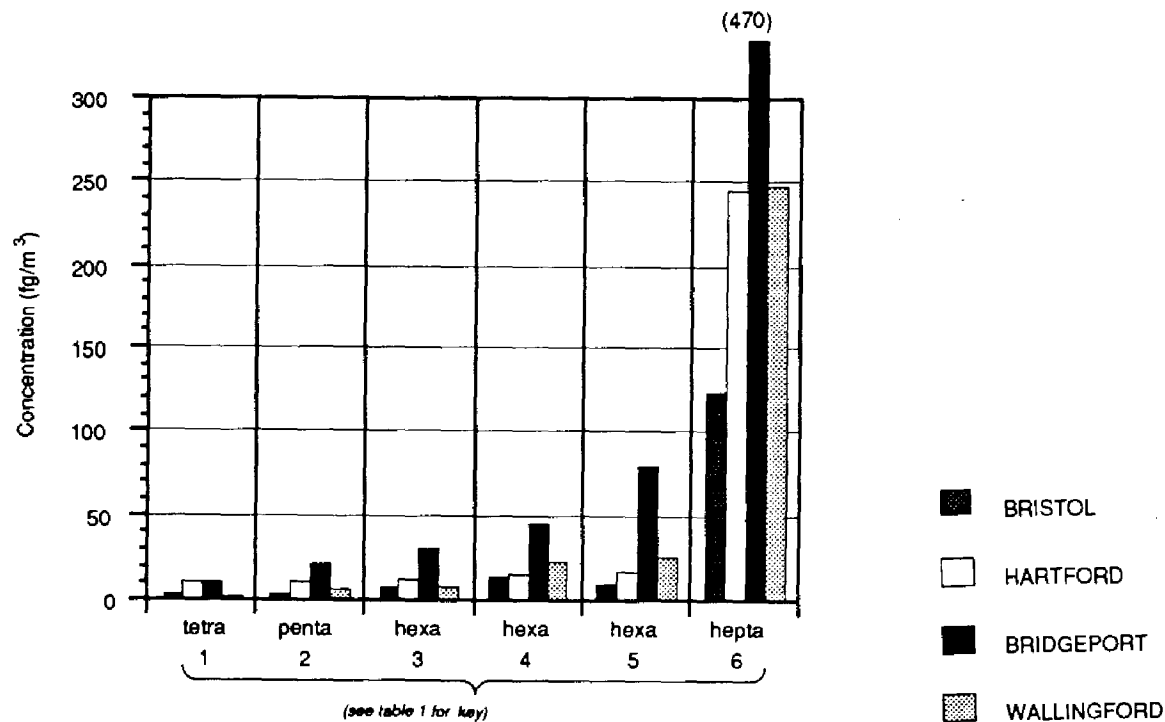
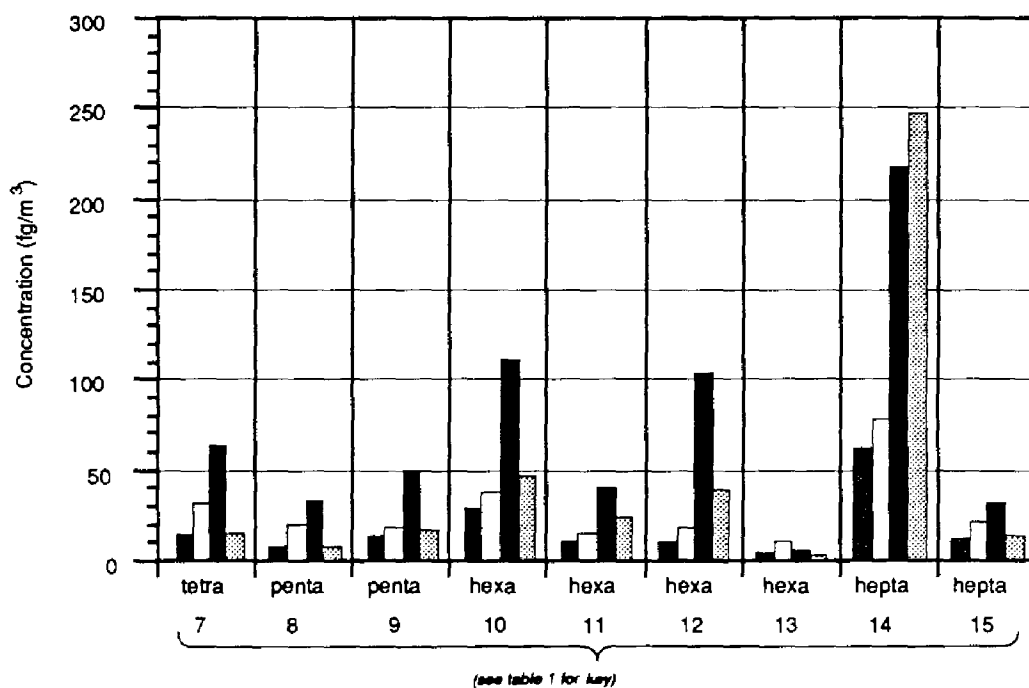


Figure 4
Average Ambient Concentrations of
2,3,7,8 - Substituted PCDFs



DEVELOPMENT AND EVALUATION OF METHODS
TO DETERMINE PATHOGENS IN AIR EMISSIONS
FROM MEDICAL WASTE INCINERATORS

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The U. S. Environmental Protection Agency has determined that medical waste incinerator emissions may reasonably be expected to contribute to the endangerment of public health and welfare. A study has been initiated to determine which air pollutants may need to be regulated under the New Source Performance Standards. One pollutant of potential concern is pathogenic microorganisms or pathogens. However, there is currently no accepted method for measurement of these emissions. An EPA-sponsored study was conducted to develop and evaluate such a method. A technique relying on measurement in the emissions of an indicator organism (the heat resistant spores of the bacteria, Bacillus stearothermophilus) spiked into the incinerated waste was selected for evaluation. Laboratory studies evaluated the precision of the proposed analytical technique, the suitability of the sampling buffer, and sample storage constraints. Field evaluation testing at a typical medical waste incinerator was used to assess the effects of sample gas components on sample recovery and the accuracy of the combined sampling and analytical procedures. This paper summarizes the results of these studies.

Introduction

The U. S. Environmental Protection Agency (EPA) has determined that medical waste incinerator emissions may reasonably be expected to contribute to the endangerment of public health and welfare. Consequently, it is anticipated that new source performance standards (NSPS) for new medical waste incinerators will be developed under Section 111(b) of the Clean Air Act. The Office of Air Quality Planning and Standards of the EPA has initiated a study to determine which air pollutants may need to be regulated. One pollutant of potential concern is pathogenic microorganisms (pathogens). As part of this study, the EPA will test a series of medical waste incinerators to determine the destruction efficiencies for pathogens under different operating conditions. A test method was required to make these determinations.

The small amount of research conducted to date has demonstrated two general approaches for measuring pathogen emissions from incinerators.¹⁻⁶ The first is to collect and culture the native species present in the stack gas and identify and quantify the same.^{4,6} The second is to spike the incinerator waste feed with an "indicator" organism (typically highly heat resistant bacterial spores), collect the "indicator spores," and then selectively culture and quantify them.^{1-3,5,6} The second approach was selected by the EPA to provide the basis for a first draft sampling and analytical protocol because (1) the incinerator is challenged with heat resistant spores simulating worst case conditions, (2) enough "indicator spores" can be spiked to ensure that the destruction efficiency of the incinerator can be demonstrated to 99.9999% efficiency, (3) the sample recovery and handling requirements are predictable, (4) the analysis of the indicator spores requires specific culturing procedures which serves to protect the analyst and minimizes sample contamination, and (5) the analysis is greatly simplified and less costly because it does not require identification of multiple species.

To summarize the first draft protocol, the incinerator is challenged with wastes spiked with a known quantity of Bacillus stearothermophilus spores. Emission samples are collected isokinetically using an EPA Method 5-type train containing a buffered impinger solution and a backup filter. The recovered sample is heat-shocked to kill non-spore microorganisms, selectively cultured for the indicator spores, and the indicator spores are quantified using a plate counting technique. Entropy Environmentalists, Inc. (Entropy) and Research Triangle Institute (RTI) conducted the laboratory and field evaluations necessary to refine the protocol and to assess its collection efficiency, accuracy, and precision.

Laboratory Evaluation

The laboratory evaluations involved confirming the selection of the "indicator" organism, determination of the analytical precision, identification of a suitable sampling buffer, assessment of sample storage constraints, assessment of the potential for background contamination, simulated sampling to estimate the accuracy of sample recovery, and design and construction of a water-cooled probe.

Bacillus stearothermophilus was selected as the "indicator spore" species for the following reasons: (1) its high relative inherent heat resistance, (2) it is commonly used in assessing sterilization processes, (3) its high culturing temperature (65°C) which excludes most other microorganisms, (4) the relative ease of culturing for counting purposes, and (5) it is not pathogenic.

Cultures of B. stearotheophilus were used to evaluate and refine the analytical techniques in the draft protocol and, in particular, to determine the precision for enumeration (counting) of the spores. Initially, an agar plate streaking technique was selected for enumeration. Briefly, this technique involves: suspending bacteria in a suitable diluent; streaking nutrient agar petri plates using a glass rod with known quantities of this suspension; counting the number of colonies which develop after incubation of the plates; and multiplying the number obtained by the dilution factor. However, a number of experiments conducted to assess the analytical precision of the techniques yielded relatively poor precisions [relative standard deviation (RSD) = 30% to 120%]. It was suspected that cell clumping and adhesion to the glass rod used for dispersal of the sample might be causing variability. The plating protocol was then modified slightly to use a solution of soft agar to disperse the sample on the plate rather than the glass rod. This technique was found unsuitable for the B. stearotheophilus because the agar melted and dripped at the high incubation temperatures. Finally, based on techniques successfully used by the Ontario Ministry of the Environment,^{7,8} an experiment was conducted to assess the precision of enumeration using microbiological filters. For this technique, known quantities of a bacterial suspension are vacuum filtered through a cellulose nitrate filter (e.g., Nalgene^R 0.2 um disposable sterile filter units); the filter is removed from the unit and placed on an agar plate; and the plate is incubated and counted as previously described. Counts of ten replicate filters yielded precisions in the range (RSD = 10% to 25%) expected for this type of measurement (RSD = 18%). Relative standard deviations from laboratory experiments conducted subsequently have ranged from 9% to 34%.

Because of the potential for high acid emissions (up to 2000 ppm) from this type of incinerator and the intolerance of the living spores for large extremes in pH, the sample collection reagent must be buffered. Work previously conducted by the Ontario Ministry of the Environment indicated that phosphate buffer could be a suitable sample collection media.⁸ It was necessary to consider sample exposure to the candidate buffer and acid catch during testing and storage of the sample in the chosen buffer solution. An experiment was designed and conducted to assess spore viability with exposure to phosphate buffers of different ionic strength and decreased pH. Each of four buffer solutions was spiked with approximately 10^3 spores of B. stearotheophilus: (1) 2.0 M phosphate buffer, pH = 6.9, (2) 2.0 M phosphate buffer, adjusted with HCl to pH = 5.7 (HCl roughly equivalent to amount collected when sampling a 1000 ppm stack for two h), (3) 0.5 M phosphate buffer, pH = 6.9, and (4) 0.5 M phosphate buffer, adjusted with HCl to pH = 5.7. Portions of the spike solutions were appropriately diluted, heat shocked, filtered, plated, and incubated to obtain a count for the spike. The spiked buffer solutions were left at room temperature for two h. Then representative aliquots were removed from each solution, heat shocked, filtered, plated, incubated, and counted. Filtration and plating of each buffer solution was performed in quadruplicate, the plates incubated overnight at 65°C, and the colonies enumerated the next day. Following removal of the first set of aliquots, the solutions were stored at room temperature. The aliquotting and analytical procedures were repeated at intervals of one, three, and seven days after spiking. There was no significant change in spore survival over a seven-day period except in the 0.5 M phosphate buffer with acid added. Therefore, the 2.0 M phosphate buffer was selected to be the sample collection reagent.

To assess the potential for contamination of emission samples from

spores in the ambient air, samples of the ambient air entering the combustion chamber were collected at two incinerator sites using midget impingers and personnel sampling pumps. For each site, three separate midget impinger trains were charged as follows: Trains 1 and 2 - 0.05 M phosphate buffer and Train 3 - 0.05 M phosphate buffer spiked with $\sim 10^3$ indicator spores. Each train collected nominally 0.2 m³ of sample during a 2-h sampling period. The impingers were sterilized by autoclaving or rinsing with 90% ethanol (EtOH) to see if a difference in the two techniques could be detected. Recovered samples were heat shocked, aliquotted, plated, incubated at 65°C, and counted after about 18 h. The results showed that there was no background contamination of any type and the use of a 90% EtOH rinse instead of autoclaving for sampling equipment sterilization did not affect the background contamination. It was concluded that background contamination is not a significant concern, however, the final draft protocol specifies collection of one background sample with each series of emission samples.

A problem anticipated with sampling in high temperature (1000°F to 2500°F) incinerator stacks using a Method 5-type impinger train is the collection of some of the spores on the walls of the probe where they would be exposed to high temperatures during the remainder of the sampling run. To resolve this problem, a water-cooled probe assembly was designed and constructed (see Figure 1). In this design, the probe liner along with an S-type pitot and a thermocouple conduit are completely jacketed by a stainless steel cylinder to allow water cooling by recirculating ice water or flow-through tap water.

Field Test Evaluation

Field evaluation testing of the candidate protocol was conducted to evaluate it under field conditions and assess the accuracy of the sampling phase. Early field evaluation testing revealed several problems with the protocol. This section begins with a description of the field evaluation test site, followed by the highlights of the problems encountered and their resolution, and is completed by a detailed description of and results from the latest field evaluation test.

A medical waste incinerator at a North Carolina hospital was selected for the method evaluation testing because (1) it is a state-of-the-art incinerator for its size, (2) of cooperation of facility personnel, (3) of its proximity to EPA/Entropy/RTI, which facilitated test program modifications, (4) it is representative of smaller hospital incinerators, and (5) it was the site of previous background contamination sampling. The unit is a Cleaver-Brooks pyrolytic incinerator with a single combustion chamber and a high-temperature (2000°F) retention chamber to increase residence time of the gases.

The samples from an initial field evaluation test revealed two problems with the sampling methodology which required correction. Immediately following the first test run conducted over a two-h period, the pH of the sampling buffer in the first impinger of each of the four trains was measured; all were pH 3 or less. Based on the buffering capacity of the sampling buffer and the volume of gas sampled, the HCl concentration in the sample gas approached 2000 ppm. The remaining sampling runs were reduced to one h to ensure that the sampling buffer could maintain the sample pH between 5.5 and 7.5; for all but one of the remaining 12 samples, it was between 6 and 7. A second problem, encountered in the course of filtering sample aliquots for analysis, was build-up of a shiny green/gray film on the filter, most likely a

by-product of the interaction of HCl in the sample gas with the stainless steel nozzle and probe liner. When a second species of spores spiked into some of the trains to assess sample recovery could not be detected on the filters, it was determined that the protocol should be modified to utilize non-metal components for all sample-exposed surfaces. A second field evaluation test revealed that if a spore spike was to be used to assess the accuracy of the sampling protocol, it would have to be introduced at the probe nozzle. Subsequent testing utilizing this spore spiking technique indicated that better spike recoveries might be possible by improving the environment in the sampling probe. This prompted development of the probe gas buffering system described below.

Sampling for the final field evaluation test involved six 30-min runs conducted over two days. The sampling train was modified to allow introduction of sampling buffer into the quartz liner of the water-cooled probe at the point of introduction of the spore spiking solution (see Figure 1). The buffer was supplied from a reservoir external to the train at a rate of approximately 20 to 30 ml/min. The volume of the first impinger of the sampling train was increased to two liters to provide capacity for the buffer introduced at the probe. Approximately 2.5×10^4 spores of B. stearothermophilus were injected into the probe through a septum over the course of each sampling run.

Prior to use, sampling equipment was rinsed with 90% EtOH. Sampling was conducted using Method 5 procedures except that it was conducted at a single point and at a constant rate based on stack conditions from previous field evaluation testing. A temperature traverse of the inside of the water-cooled probe was performed under sampling conditions. An extra impinger containing 100 ml of sampling buffer was placed prior to the silica gel impinger for two of the six runs. The contents of this impinger were recovered and analyzed separately to determine the sampling train collection efficiency. Analysis of each sample involved (1) heat shocking to eliminate non-spore microorganisms, (2) aliquotting of the sample into 1-, 10-, and ~100-ml portions, (3) vacuum filtration through 0.2 μ m cellulose nitrate filters, (4) agar plating of filters, (5) incubation of filters at 65°C, and (6) enumeration of the colonies on the filters. The recovery of the spiked spores was calculated as a percentage of the original spike amount indicated by the control sample. The precision of the sample analysis was expressed as a relative standard deviation between the results for replicate aliquots.

The spore spike recoveries (or method accuracy) ranged from 37% to 133% and centered around 60%. The RSDs for the 10-ml aliquots ranged from 3% to 90% and were typically 5% to 30%; the RSDs for the 1-ml and nominally 100-ml aliquots were significantly higher. The nominally 100-ml aliquots (~75 ml for the probe rinse samples and ~600 ml for the impinger samples), yielded colonies which were more irregular, harder to see, more difficult to count, and often more prevalent away from the ash particles caught on the filter. They also showed reduced sample recoveries compared to the 10-ml aliquots, possibly as a result of growth inhibition caused by the ash. The 1-ml aliquots showed more variability as would be expected, because the spore counts were closer to the detection limit of the analytical technique. No colonies and only two colonies were present on the filters from the extra impinger samples. This represented significantly less than one percent of the total spore sample indicating good collection efficiency and justifying elimination of the backup filter from the candidate train. The temperature traverse demonstrated a rapid reduction in sample gas temperature from 1850 °F at the entrance to the probe to 70°F at the first impinger. The probe buffering system was shown to be of benefit in improving the spike recoveries.

Conclusions

Considering that the candidate protocol will be used to calculate a destruction efficiency which is an order of magnitude measurement, the method accuracy of approximately 60% is adequate for the purposes of the method. The final draft method reflects the results of the laboratory and field evaluation testing and incorporates these key elements: a water-cooled quartz-glass probe with buttonhook nozzle and probe gas buffering system; a large first impinger to provide a reservoir for the introduced buffer; measurement of the first impinger pH; an incinerator waste spike of at least 10^{12} indicator spores; disinfection/sterilization of the sampling train components using ethanol; use of a 2.0 M phosphate buffer impinger solution; use of the filtering technique for spore enumeration; collection of a background sample; and aliquotting of the sample to minimize matrix interference, provide measurements in a suitable analytical range, and provide an indication of analytical precision.

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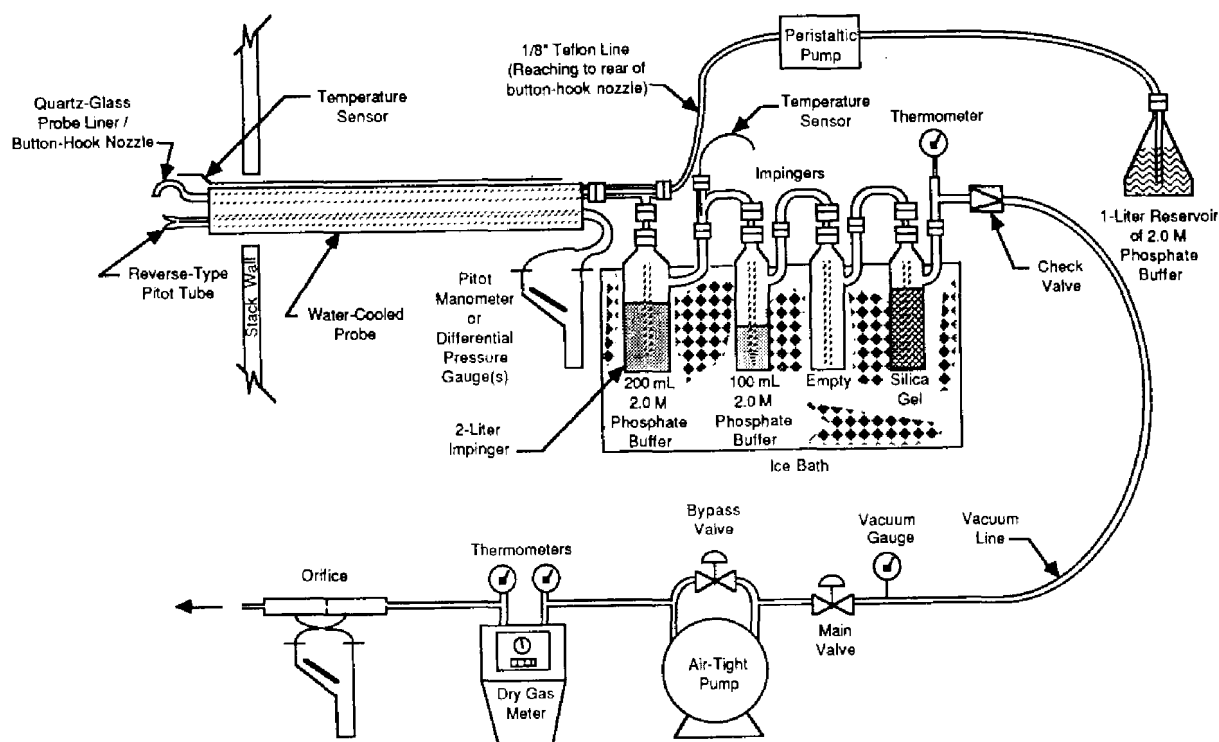


Figure 1. Schematic of sampling train for determining pathogen destruction efficiency.

PRIORITY POLLUTANT METALS IN RESPIRABLE AND
INHALABLE (PM₁₀) PARTICLES

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Respirable (<2.5 μ) and inhalable (<10 μ) particles have been collected from over eighty area and point sources in California, Colorado, and Montana. These sources have included a variety of industrial stacks, windblown and road dusts, vehicular exhausts, residential wood combustion, and emissions from agricultural activities. Custom sampling procedures have been developed for the collection of representative samples from each of the sources. Dilution tunnel sampling, ground-based fugitive emission sampling, and bulk sampling/resuspension protocols have been established. Multi-element analysis has been conducted for thirty-eight elements by x-ray fluorescence spectrometry. Among the elements measured, the priority pollutant metals of antimony, arsenic, cadmium, chromium, copper, lead, mercury, nickel, selenium, silver, thallium, and zinc were quantified. The sampling and analytical methods which have been developed are discussed and a comparison of priority pollutant metal concentrations for selected sources is presented.

Introduction

Priority pollutants are listed in Section 307(a)(1) of the 1977 Clean Water Act. Among the 129 priority pollutants listed in the Act are 13 metals. These priority pollutant metals are antimony, arsenic, beryllium, cadmium, chromium, copper, lead, mercury, nickel, selenium, silver, thallium, and zinc. Subsequent to their listing in the Clean Water Act, they have been used as target metals to assess pollution in all media and are, for example, listed as hazardous substances in response to CERCLA (40 CFR Section 302.4).

Emission rates of priority pollutant metals from point, area, and fugitive aerosol sources are frequently of concern. Similarly, the documentation of metal concentrations in airborne particles in indoor and outdoor environments has been the subject of numerous investigations. Assessments of environmental impacts, community-wide health risks, industrial exposure and regulatory compliance often require their measurement.

During the last decade, chemical mass balance (CMB) modeling for air pollutant source identification and apportionment has gained wide acceptance. To support this air quality model, specialized sampling instrumentation, protocols, and analytical procedures have been developed to accurately quantify multiple pollutants emitted from aerosol sources. Among the 13 priority pollutant metals, 12 have been routinely and accurately measured as part of the process. (Only beryllium is not routinely measured.) Numerous CMB source profile libraries have been compiled listing, among the measured constituent, the 12 metals.

A description of the sampling instrumentation, protocols, and analytical procedures appropriate for accurate priority pollutant metal quantification in $PM_{2.5}$ and PM_{10} particles from a variety of source types is presented in this paper. In addition, some representative data contained in CMB source profile libraries prepared from work conducted in California, Colorado, and Montana are presented.

Methodology

The objective of aerosol sampling and analysis for the development of source profiles for use in CMB modeling is to obtain an accurate and representative chemical composition. A streamlined set of sampling, analysis, and data reduction protocols has been developed to achieve this objective.¹ Since the physical and chemical environments encountered during source sampling differ from source to source, several source sampling instrument systems and protocols have been developed. In terms of sampling requirements, sources can be grouped into three major categories. These are: (1) point and combustion sources; (2) process fugitive sources; and (3) passive fugitive sources.

Point sources (including combustion sources such as residential wood combustion [RWC] and vehicular exhaust) represent a special problem for source sampling. The alteration in particulate chemistry and size distribution which occurs when high-temperature emissions cool and mix with ambient air requires that a dilution/cooling tunnel be used prior to aerosol sample collection. Condensation, agglomeration, volatilization, and secondary chemical reactions can all modify the character of source particles. A number of dilution source sampling instruments have been developed². Factors taken into consideration in dilution source sampler designs include variable dilution ratios, interfacing with size-categorizing equipment, portability, inert construction materials,

isokinetic sampling, and the ability to be assembled in a variety of geometric configurations to conform to real-world space constraints. A detailed description of a dilution source sampling system which has been used to sample numerous sources is presented in reference 3.

Process fugitive sources have been sampled in two general ways. These are (1) custom siting of ground-based sampling equipment or (2) plume sampling with balloons or aircraft. Unducted emissions from industrial complexes, intermittent emissions from slag pouring, and dust generated by heavy industrial equipment, are examples of process fugitive sources. Instrumenting requirements can be as simple as using commercial ambient samplers, perhaps placed on a platform or tower, or as sophisticated as custom-designed, ultra-lightweight samplers for use with helium balloons.⁴ A key criterion for sampling process fugitive emissions using either ground-based or airborne samplers is that the source of interest dominates the particle concentration during sample collection.

The passive fugitive dust category for the purposes of source sampling strategies can be either wind-blown dust from open areas or suspension of particles by traffic or heavy equipment. Detailed standard protocols have been developed for the sampling and analysis of such dust.⁵ Sampling protocols include procedures for (1) sampling paved roads; (2) sampling unpaved areas which have a surface layer with a distinct chemical character due to anthropogenic impact (e.g., unpaved roads and parking lots); and (3) sampling of dust sources with a relatively homogeneous near-surface chemical composition (e.g., tilled agricultural soils, native soils, and bulk storage piles). While the actual physical collection of the dust samples is relatively simple, ensuring representative samples is not. Compositing samples is a useful technique to ensure that representative chemical source profiles are produced. Collection of sub-samples at regular intervals along a roadway or at various points in an agricultural field or from different storage piles is a reasonable approach to compositing. Once bulk samples are collected, laboratory drying at low temperatures, sieving, resuspension, and particulate collection with size-segregating samplers can be conducted.³

A variety of analytical procedures have been developed to chemically characterize the particulate material contained in source samples. Most useful for priority pollutant metals is x-ray fluorescence spectrometry (XRF), which can quantify all priority pollutant metals except beryllium. While the detection limit of the technique varies from element to element and depends on the mass loading as well as the overall chemical matrix, the detection limits are typically at the hundredth-of-a-percent level.

Results and Discussions

Table I lists priority pollution metals in PM_{10} particles from a number of sources compiled as part of CMB source profile libraries.^{3,6,7} Uncertainties and detection limits listed in Table I are not only due to the analytical techniques, but represent sample variability in replicate samples or sequential sampling runs. In addition, some of the values, propagated uncertainties, and detection limits were produced by "blending" results from individual sub-classes of emissions. For example, the vehicular exhaust data are a blend of unleaded, leaded, and diesel emissions (30%, 20%, and 50%, respectively) and the RWC data are a blend of emissions from a number of woodstoves and fireplaces.

Upon review of the data that has been compiled in the various source libraries,^{3,6,7} two key observations can be made. One is that many indiv-

idual sources can have specific priority pollutant metals in PM_{10} particles at the percent level. For example, as illustrated in Table I, mercury from municipal garbage incineration, zinc from combustion of wood in hog fuel boilers, and nickel from crude oil combustion can all be above the percent level in PM_{10} particles. The other observation is that some of the priority pollutant metals occur at above detection limits in ubiquitous area sources such as road dust, agricultural dust, and vehicular exhaust. The metals of copper, chromium, and nickel are at low but measurable concentrations in dusts, which can be due simply to their crustal abundance. Lead and zinc in urban road dust are, on the other hand, clearly anthropogenic in origin, and are from the use of leaded gasoline and tire wear. Interestingly, and notable in terms of human health impact, lead and zinc collected in urban road dust is most highly enriched in respirable ($PM_{2.5}$) or finer particles (Figures 1 and 2).

In summary, source sampling methods and analytical procedures have been developed in the past ten years to accurately measure priority pollutant metals in PM_{10} as well as other size particles from particulate sources. While the sampling and analytical activities have been primarily to support CMB modeling, the same techniques can be used for measuring priority pollutant metals for the evaluation of health and environmental impacts. In addition, published CMB source profile libraries can provide an existing and useful data base for such evaluations.

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Table I. The priority pollutant metal content of PM₁₀ particles from selected sources¹.

Priority Pollutant Metal	Area Sources				Point Sources			
	Urban Street Dust (Fresno, CA)	Agricultural Soil Dust (Visalia, CA)	Vehicular Exhaust ² (30% unleaded, 20% leaded, 50% diesel; Denver, CO)	Residential Wood Combustion (Denver, CO)	Garbage Incinerator (CA)	Hog Fuel Boiler (MT)	Crude Oil Combustion (Steam Injection; Kern R. Oilfield)	Coal Combustion ² (Baghouse; Denver, CO)
Antimony	<0.03	<0.01	<0.08	<0.01	<0.1	<0.01	<0.01	<0.08
Arsenic	<0.04	<0.003	<0.21	<0.002	<0.03	0.029±0.004	0.019±0.002	<0.02
Cadmium	<0.02	<0.008	<0.04	<0.008	<0.06	<0.009	<0.005	<0.05
Chromium	0.030±0.003	0.030±0.003	±0.01	<0.001	0.04±0.02	0.004±0.001	<0.03	0.015±0.004
Copper	0.020±0.002	0.006±0.001	±0.01	<0.001	0.04±0.01	0.042±0.003	±0.01	0.02±0.01
Lead	0.26±0.03	0.010±0.001	1.3±0.4	<0.003	0.16±0.04	0.071±0.006	<0.003	0.10±0.02
Mercury	<0.008	<0.003	<0.02	<0.003	1.1±1.0	<0.002	<0.002	<0.02
Nickel	0.011±0.001	0.006±0.001	<0.07	<0.005	0.014±0.006	0.0013±0.0003	2.6±0.3	0.008±0.002
Selenium	<0.002	<0.001	<0.01	<0.001	<0.007	0.0026±0.0007	0.027±0.004	0.007±0.003
Silver	<0.02	<0.008	<0.04	<0.007	<0.06	<0.008	<0.004	<0.04
Thallium	ND	ND	ND	ND	ND	<0.003	ND	ND
Zinc	0.17±0.02	0.026±0.002	0.11±0.06	<0.04	0.5±0.2	1.22±0.09	0.02±0.01	0.08±0.05

1. All values are weight percent; each source profile is a mean of numerous samples or a "blend" of various individual profiles. Uncertainties are propagated values, not analytical uncertainties.
2. The vehicle exhaust and coal combustion values are for PM_{2.5}.

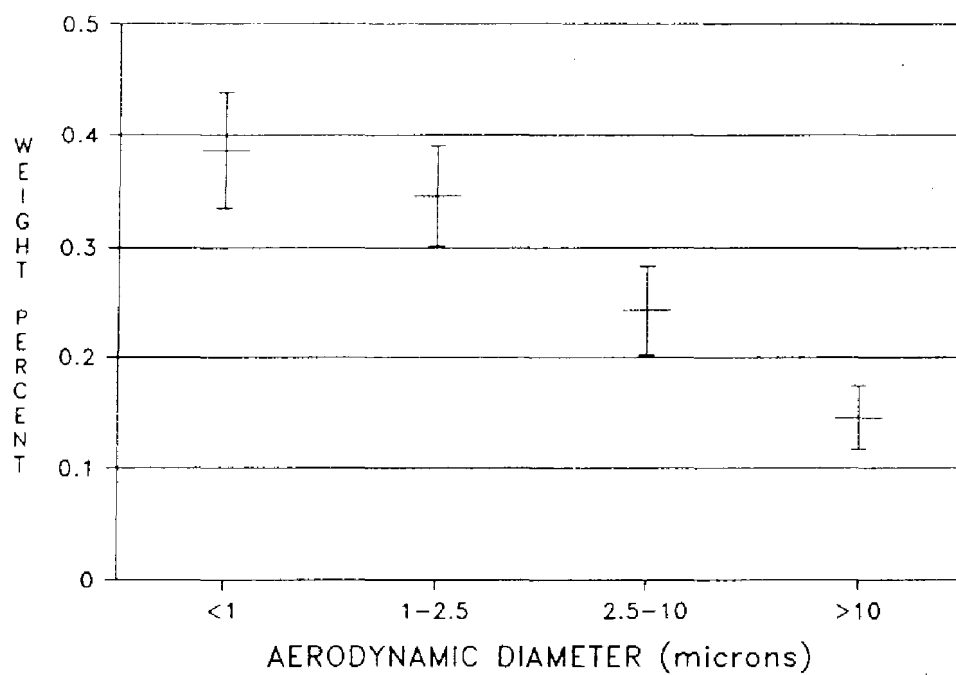


Figure 1 Weight percent lead vs. size categories for urban road dust.

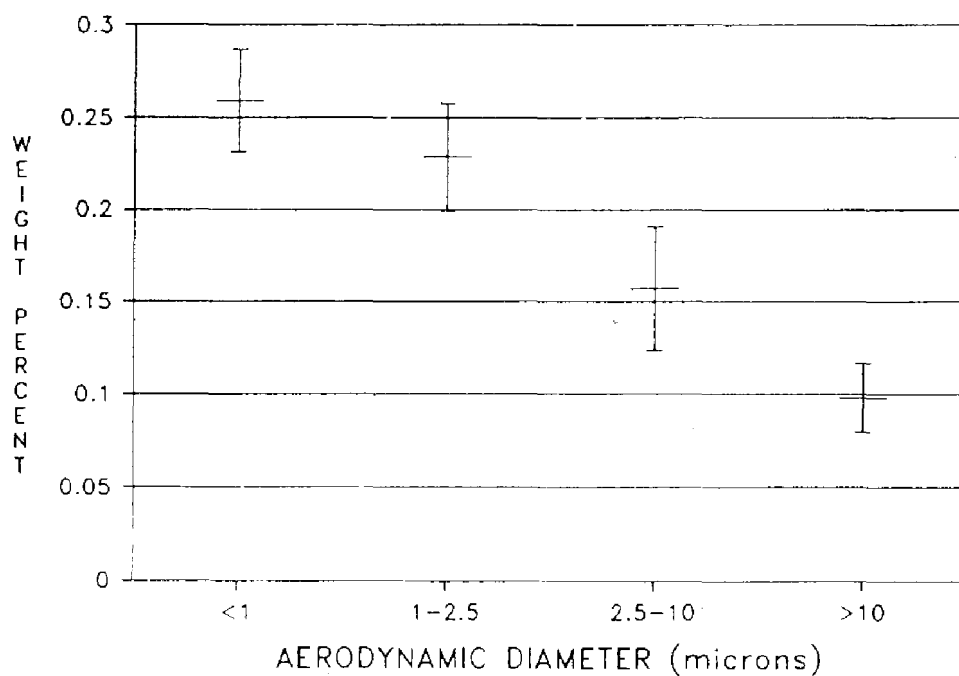


Figure 2 Weight percent zinc vs. size categories for urban road dust.

ATMOSPHERIC TRANSPORT OF TOXIC CHEMICALS AND THEIR POTENTIAL IMPACTS ON TERRESTRIAL VEGETATION: AN OVERVIEW

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Numerous anthropogenic sources emit a large variety and quantity of toxic chemicals into the atmosphere. Through the processes of atmospheric transport and deposition, toxic chemicals have found their way to remote environments far from emission sources. Recent data strongly suggests that the enriched concentrations of several contaminants detected in the air, water, soil and biota of rural and remote environments are the result of long-range atmospheric transport from sources located in temperate and sub-tropical latitudes of North America and Eurasia. Many of these chemicals are persistent, bioaccumulate and remain biologically harmful for long periods of time. Although air toxics have been primarily considered an urban health problem, there is increasing concern among scientists that adverse ecological impacts may result from their deposition into terrestrial ecosystems and their subsequent exposure of plants. The chronic exposure of vegetation to low concentrations of air toxics may result in sublethal effects such as decreased plant productivity and vigor, which may culminate in changes in plant communities and ecosystem structure, composition and function. This paper will present an overview of air toxics emissions, atmospheric transport and deposition, their potential effects on terrestrial vegetation, and recommend research needs.

Introduction

Airborne pollutants can be broadly defined as any chemical occurring in the atmosphere that may pose a threat to human health or the environment. This broad definition includes an array of chemicals ranging from the well-studied criteria pollutants to the less-studied radiatively-important trace gases. However, to provide a more focused definition for this paper, air toxics refers to the following groups of airborne substances: (1) synthetic industrial organics, (2) agricultural pesticides, (3) trace metals, (4) organometallic compounds, and (5) non-metallic inorganics.

Since the release of the Environmental Protection Agency's Toxic Release Inventory estimates for 1987¹, there has been a heightened concern over the nation's air quality. Primarily this concern has been directed at human health effects in industrial-urban areas. The fact that many airborne chemicals pose hazards to human health is only one aspect of the problem. The continued deposition of airborne toxic chemicals on a regional to global scale will impact public welfare if it results in adverse impacts to the structure and function of sensitive terrestrial and aquatic ecosystems. Although airborne toxic chemicals pose threats to both terrestrial and aquatic ecosystems, this paper will limit its discussion to terrestrial vegetation.

Emission Sources

Airborne chemicals are emitted into the atmosphere from a large number and variety of point- and area-sources. Anthropogenic emissions emanate from industrial, urban and agricultural sources such as chemical, metal, plastic, and paper/pulp industries; fossil fuel processing plants; motor vehicles and aircraft; municipal waste incinerators; agricultural practices such as pesticide usage and field burning; and small businesses such as dry cleaners. Emissions of toxic chemicals into the atmosphere may occur directly by the deliberate or inadvertent releases from industrial or urban sources, or indirectly through volatilization following the deliberate or accidental discharge of chemicals into water or soil resources. Also, considerable amounts of toxics enter the atmosphere from wind drift and volatilization after agricultural chemical applications.

Industry is probably the major anthropogenic source of airborne toxic chemicals. Approximately 65,000 chemicals are used worldwide for industrial purposes.² Many of these chemicals eventually are emitted into the atmosphere. The 1987 Toxic Release Inventory (TRI) reported that industries within the United States emitted over 1.2 billion kilograms of toxic chemicals into the atmosphere.¹ The TRI underestimated the actual air emissions as it did not include air emissions from numerous area sources (e.g., agriculture, households, motor vehicles), industrial categories such as petroleum tank farms, companies with less than 10 employees, or urban businesses (e.g., dry cleaners).

A secondary source of airborne toxics is the application of pesticides. Atmospheric loads of pesticide residues resulting from wind drift, as well as volatilization from soil and plant surfaces after their application to agricultural, forest, industrial and household lands are likely significant. Over 455 million kilograms of pesticide active ingredients are used annually on 16% of the total land area of the United States.³ Agricultural lands account for approximately 75% of the pesticide usage in the United States. The magnitude of pesticide active ingredients entering the atmosphere during and following application are poorly known, but are estimated to range between 30-55%.⁴

Atmospheric Processes

Once chemicals are airborne, they are subjected to the prevailing atmospheric conditions. Wind, precipitation, humidity, clouds, fog, solar irradiation, and temperature influence the environmental fate of air toxics.^{2,5} The complex reactions within the atmosphere that are driven by chemical processes such as hydroxyl scavenging or solar irradiance may result in the formation of products that can be as toxic or more so than the parent compounds. On the other hand, transformation reactions may also render a toxic substance harmless.

The atmosphere is a major pathway for the transport and deposition of the air toxics from emission sources to the terrestrial ecosystem receptors - vegetation and soil.⁵ The prevailing meteorological conditions and the physio-chemical properties of the chemicals will dictate atmospheric residence times and deposition velocities to the receptors.² Atmospheric residence times depend on such characteristics as mode and rate of emission, atmospheric transformations, physical state (gas, solid, liquid), particle size and chemical reactivity.² Thus, airborne pollutants may be deposited close to their sources or be carried great distances before being deposited into remote ecosystems.

The movement of airborne chemicals downwind from point sources has received a great amount of attention since the early 1900's due to the damaging effects on vegetation that occurred within the plumes.⁶ During the last 10 to 20 years, however, the phenomenon of long-range atmospheric transport has been implicated in the wide distribution of anthropogenic contaminants on regional and global scales. Industrial organic compounds, trace metals and pesticide residues have been detected in the vegetation of remote terrestrial ecosystems such as the Arctic,⁷ Antarctic,⁸ forests,⁹ and peatlands.¹⁰

Environmental Partitioning and Vegetation Exposure

Terrestrial plants are exposed to toxic chemicals through the environmental media of air, water and soil. The atmosphere, however, is of prime importance due to its potential for pollutant dispersal on a regional to global

scale, its ability to move pollutants rapidly, and its dynamic nature. After pollutant deposition to terrestrial ecosystems, the fate of the toxic compounds depends on their partitioning coefficients.

The environmental partitioning of pollutants within ecosystems will dictate their potential ecological impact to vegetation and other biota.¹¹ For example, trace metals tend to accumulate on soil surfaces via their adsorption to organic matter. Trace metal accumulation may reduce plant growth and vigor through the disruption of nutrient uptake by the roots and decreased organic matter decomposition. Gaseous chemicals reside in the atmosphere with the potential to disrupt plant-leaf biochemical processes after absorption through the stomata or cuticle. Because of the lipophilic nature of many synthetic organics, the waxy cuticle of vegetation may accumulate high levels of these substances. Transfer of toxic chemicals among ecosystem compartments will occur. Trace metals may be absorbed by plant roots or deposited onto the leaves and then transferred to the soil through deciduous tissue loss and decay. Contaminants may be passed along food chains through herbivory with the potential for biomagnification. The deposition of airborne toxic chemicals into agricultural ecosystems has the potential to contaminate human food resources.

Impacts on Terrestrial Vegetation

Scientists have recognized that airborne pollutants can adversely impact agricultural and natural plant communities by reducing plant production and altering successional pathways.^{11,12} Emissions of sulfur dioxide, hydrogen fluoride, trace metals and other toxics from pulp and paper mills, ore smelters, and power plants have severely reduced vegetation cover, biodiversity and ecosystem integrity downwind from point sources.^{6,12} In addition to local plume effects, atmospheric pollutants can also cause regional damage to plant communities through exposure to chemical oxidants such as ozone and peroxyacetyl nitrates or acid precipitation.^{12,13}

The potential biological effects of air toxics on terrestrial vegetation are numerous and mediated through individual plants to the community and ecosystem.¹¹ The type and magnitude of these effects will depend on the pattern of exposure (e.g., duration, concentration, frequency, season) individual plants receive, their sensitivity to the pollutant, and the phytotoxicity of the chemical. When an airborne toxic chemical is introduced into a plant community some plants will be more affected than others depending on individual tolerances endowed by their genotype, as well as their phenology and various modifying microclimatic variables. The sensitive plants or species are no longer able to compete adequately with the tolerant plants or species and will be partially or completely replaced. Those plants that survive and persist in contaminated habitats are the result of their tolerance or microhabitat protection.

After pollutant absorption by the plants through the leaves or roots, biochemical processes are the first site of action. If enzymatic degradation detoxifies the pollutant then no injury will occur. However, if enzymatic action cannot render the pollutant or its metabolites harmless, then alterations in plant metabolism may result in foliar injury, altered carbohydrate and nutrient allocation, reduced growth and reproductive capability¹³. The degree of impact to the plant will depend on the toxicity of the pollutant and its exposure pattern. Acute exposures usually cause observable morphological damage, such as leaf lesions, stunted growth or even death. Plant death resulting from acute exposure is usually localized when it does occur; resulting from an inordinate amount of toxic chemical exposure via an accidental release or pesticide wind drift.

However, chronic, sub-lethal exposures may not induce observable morphological damage, but rather alter biochemical pathways which can result in decreased vigor and productivity, altered phenology, loss of tissue or reduced reproductive potential. Altered physiological processes will cause a loss of vigor and render the plant more susceptible to insect damage or disease. Decreased reproduction will impact the population through the loss of new recruitments to the plant community. With continual exposure, even at sublethal concentrations, sensitive plant populations may decrease in numbers allowing tolerant species to become dominant. Thus, shifts in plant community structure and composition could result in decreased biological diversity and altered ecosystem functions.

Plant damage resulting from acute air toxic exposures are usually limited in time and space as a result of control technology and legislation. However, sublethal, long-term plant exposure to airborne pollutants may predispose vegetation to other natural stressors and induce damage or mortality. Even though air toxic damage may not cause permanent functional loss, the diversion of biochemical resources to repair the injury will inhibit normal plant functions. Thus, air toxic induced physiological stress may predispose a plant to other stressors such as frost, drought, insects, or disease. Some scientist propose that the widespread forest tree decline is not the result of a single agent but an interaction among chronic exposures of air pollutants and natural stresses.

Air toxics may also pose indirect effects on vegetation by directly affecting other organisms which are critically associated with the plants. Soil microorganisms and invertebrates are critical in ecosystems for litter decomposition and nutrient cycling. An accumulation of trace metals within the "O" horizon of the soil may limit organic matter decomposition and nutrient availability to plants. Many plants rely on insects for pollination. Airborne pollutants from the use of insecticides can reduce non-target insect populations, resulting in inadequate flower pollination and subsequent seed set.

The effects caused by air toxics on vegetation can be extended to the animals within the ecosystem. Reduced plant cover and habitat quality will result in animals being more susceptible to predation and disease. Adequate birthing sites may be reduced because of changes in vegetation structure and cover. Animal forage that is contaminated may result in decreased population size or starvation. Toxic chemicals may be passed along food chains with the potential to reduce the health of herbivores or bioaccumulate within predators. Animal populations will respond to such habitat changes through decreased reproduction, emigration or mortality. Even though the populations of certain species may increase because of habitat changes that are favorable to them, the biological diversity of the overall ecosystem will still decrease.

Research Needs

Air toxic chemicals introduced into plant communities can cause effects ranging from the biochemical level to changes in plant community structure and composition. The effects of acute exposure to plants are well documented. However, a paucity of information exists on the effects of long-term, chronic exposures of air toxics to vegetation. Several areas of research would provide data to quantify vegetation responses to chronic air toxic exposure:

1. Given the large number of toxic chemicals emitted into the atmosphere, research is required to identify and prioritize the most critical airborne contaminants and sensitive ecosystems. A comprehensive computer-based system would be useful for conducting preliminary risk assessments of the numerous airborne toxic chemicals and their effects on vegetation and provide research guidance.
2. Quantify and model the exposure, deposition velocity and absorption of air toxics to plants.
3. Determine the biochemical and physiological responses of plants to chronic exposures to air toxic chemicals and develop exposure-response functions. This research then could be extended to quantify the response of plant populations and simulated plant communities.
4. Initiate long-term studies to determine sensitive elements of plant community structure and function that would lead to significant change and degradation from air toxic exposure. This research would identify unacceptable change in plant communities and identify early warning signals.

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FLUORIDE PHYTOTOXICITY: PAST, PRESENT AND FUTURE

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Fluoride is markedly more phytotoxic than any of the major air pollutants and its deleterious effects on crops, forests and other vegetation have been chronicled for more than a century. Plants can also serve as vectors for the transfer of fluoride from the atmosphere to animals. The accumulation of high concentrations of fluoride in foliar tissues may be hazardous if ingested by herbivores. During the past two decades, improvements in emission control technology have dramatically reduced the incidence and severity of fluoride-induced plant damage. These reductions have shifted the emphasis of environmental concerns from the direct to the indirect and subtle effects of fluoride on vegetation, plant communities and even ecosystems. This review, in addition to providing a summary of the direct and indirect effects of fluoride on plants, also includes information on the factors that alter the plant's responses to exposure. The aim of future research will be to provide the information necessary to establish realistic air quality guidelines or standards for atmospheric fluoride that will allow industry and agriculture/forestry to coexist.

INTRODUCTION

Of the major air pollutants, fluoride is the most toxic to vegetation and its deleterious effects have been the subject of controversy and concern for more than a century. The extent and severity of the problems associated with atmospheric fluoride increased with industrialization, peaked during and after World War II, and then, with the imposition of governmental regulations and improvements in emission control technologies, diminished. Research efforts closely paralleled this progression and were largely responsible for the actions taken to cope with it.

These investigations included: (i) vegetation surveys around sources where plant injury occurred; (ii) experimental exposures to atmospheric fluoride to reproduce and validate the symptoms observed; (iii) development of methods to monitor fluoride in the air and measure its accumulation in plants; and (iv) controlled exposures to determine the relative susceptibility of various plant species, dose-response relationships, and the factors that can alter or modify the plant's response to fluoride.¹

A synthesis of the historical aspects of the growth and diminution of the impacts of atmospheric fluoride on vegetation provides a useful example of how a major environmental problem can be dealt with. Thus a review of this kind serves two purposes. First, it sheds light on the fluoride-vegetation problem *per se*; the sequential events leading to plant responses and the consequences of these effects with respect to impacts on growth, quality and yield. Second, it illustrates how the joint contributions of science, technology, and policy can contribute towards the solution, at least in part, of a major environmental problem.

THE PROBLEM

Toxicity

Air pollutants such as ozone and other oxidants, sulfur dioxide, and oxides of nitrogen are more important than airborne fluoride with respect to their total economic effects on crops, forests and indigenous vegetation. Although fluoride is ranked lower in terms of economic losses, on a concentration basis it is one to three orders of magnitude more phytotoxic than any of those air pollutants.²

Plants are considerably more susceptible to fluoride than man or other mammals. For example, the OSHA standard for man in the workplace environment is 2.5 mg F m^{-3} for eight hours daily, five days per week over the working lifetime of a healthy adult. At this level of exposure it is presumed that no deleterious effects on human health will occur. For plants, however, the limits are much lower and air quality standards or guidelines to protect vegetation have been adopted by several states in the U. S. and provinces in Canada. The units of measure for these are not as 'mg', but as ' μg ', and range from limits of less than $4 \mu\text{g F m}^{-3}$ for 12 hours down to a mean concentration of less than $1 \mu\text{g F m}^{-3}$ over 30 days.

In addition to the direct phytotoxicity of fluoride, vegetation can also serve as the means for transferring fluoride from the atmosphere to animals. Plant foliage may accumulate atmospheric fluoride to concentrations that may be injurious to livestock that consume it.³

For these reasons, regulations to limit the harmful effects of fluoride usually consist of one or more of three approaches: (i) restrictions of emissions at the source, (ii) ceilings on the maximum allowable air concentrations or doses, and (iii) limits for the concentrations of fluoride in vegetation, especially forages.

Sources

Sources of fluoride for plant uptake are soils, water and air, and fluoride phytotoxicity is usually ascribed to the airborne fraction.⁴ Soils and waters naturally contain fluoride to some degree, and this accounts for the concentrations found in plants grown where there are no atmospheric fluorides. Background concentrations are usually low (<20 ppm), but some plants are known to be "accumulators". Species of *Camellia*, *Deutzia*, and to a lesser degree *Gossypium*, *Carya* and *Cornus*^{5,6} normally accumulate from the soil high concentrations of fluoride in their leaves (60-1370 ppm) while other plants in the same environment take up very little. These "natural" accumulations of fluoride rarely, if ever, affect the plant *per se*, but if sufficiently high they may be harmful when consumed by herbivores. Phytotoxic responses to more susceptible plants do occur, however, when elevated concentrations of fluoride in foliage are derived from exposures to fluoride in the atmosphere.⁴

Natural sources of gaseous and particulate fluorides in the atmosphere include volcanoes and fumaroles⁷, and these may cause serious damage to plants, animals and ecosystems. This review, however, will concentrate on airborne fluorides of anthropogenic origin. Essentially all industrial processes that utilize fluoride-containing substances as raw materials or as fluxes, catalysts, etc. are potential sources of emissions of fluoride to the atmosphere. Some examples are aluminum smelting, coal combustion, the manufacture of phosphoric acid, phosphate fertilizers and feeds, steel, glass and frit, and brick and ceramic products.⁴ The amount and composition of fluoride emissions from a source will depend on the kinds and amounts of material manufactured, processed or consumed and the efficiency of effluent controls.

Historical

The earliest reports of effects on vegetation, that have subsequently been ascribed to fluorides, were associated with volcanic activity in Iceland more than 1,000 years ago. More recent records from eruptions of Mt. Hekla in the 17th, 18th and 19th centuries describe catastrophic effects on plants, animals and entire ecosystems from the immediate effects of gaseous hydrogen fluoride (HF) and the lingering effects of fallout of fluoride-containing ash.⁷

The main focus of this paper, however, is fluoride of anthropogenic origin. Confirmed cases of injury to vegetation from industrial emissions began to appear in Europe in the late 1800s. Copper smelters, superphosphate factories and glass works were the sources of these early incidents and the involvement of fluoride was confirmed initially by leaf analysis and later by experimental exposures to HF.⁸ In the United States significant problems were first detected during World War II with the rapid expansion of aluminum production to supply aircraft and other wartime needs; pollution control had low priority. Post-war growth of aluminum smelting and of the production of phosphate and superphosphate fertilizers increased fluoride emissions to the atmosphere; but the increases were not proportional to production as the installation of scrubbing equipment was beginning to take hold. Nevertheless, the post-war period saw many complaints for damages to vegetation that resulted in significant and extended lawsuits. Evidence presented in the trials revealed that there was little reliable information about the effects of fluoride that either side could rely on. Both government and industry began to support investigations to meet these needs and by the late 1950s research programs were in place at several universities and institutions.⁹ Several of these programs are still in existence, and some of the concepts revealed by research are summarized below.

DIRECT EFFECTS ON VEGETATION

Uptake

All plant surfaces are capable of intercepting and adsorbing both gaseous and particulate fluorides. Gaseous forms readily enter the plant by diffusion through stomata. Forms resident on leaf surfaces may penetrate the cuticle, but this is a relatively slow process and its rate is dependent on the solubility of the adsorbed fluoride and the physical and chemical characteristics of the foliar surface.^{5,10} A significant proportion of fluoride-containing particulate material deposited on leaves does not penetrate.

Once fluoride has entered the leaf it dissolves in plant fluids and is translocated acropetally via the transpiration stream to the margins and tips of leaves where it accumulates and, as water is lost, concentrates. When toxic concentrations are achieved, injury occurs.⁵

Progression of Effects

The initial fluoride-induced changes that occur within cells include altered metabolism, distortions and disruptions of organelles, and breakdown of the tonoplast and other membranes.¹¹ Effects at each level of organization may affect the next higher level. For example, cellular changes lead to symptoms and reduced assimilatory capacity of leaves, and foliar injuries can result in effects on growth or reproduction of the entire plant.⁴

Symptoms

The most obvious effect of fluoride on the plant is foliar injury, which has long been used for diagnosis and evaluation in the field. Chlorosis from the direct effects of fluoride on chlorophyll synthesis, and necrosis from the death of groups of cells are the most common symptoms,¹¹ but deformations from uneven leaf growth are also associated with fluoride injury. The degree and pattern of leaf injuries are dependent on the relative susceptibility of the plant and how the fluoride was accumulated. Symptoms from chronic (long-term, low concentration) or recurrent exposures are quite different than those induced by acute (short-term, high concentration) exposures. For example, in chronic exposures where uptake and translocation are in balance, chlorosis and necrosis first appear in apical and marginal areas of young, expanding leaves. During acute exposures, which rarely occur in the field, uptake exceeds transport resulting in toxic concentrations in localized areas of the leaf where irregularly-shaped necrotic lesions develop.¹

Growth and Yield

Fluoride-induced chlorosis may result in altered growth through reductions in the rate or efficiency of photosynthesis. Foliar necrosis reduces the area of photosynthetically active tissue and consequently may affect growth and yield.^{11,12} However, reductions in foliar surface area from exposure to fluoride or even from clipping do not always affect growth and reductions in growth can occur without the concomitant appearance of foliar symptoms.

The effects of fluoride on yield and on foliar injury are for some plants independent. Exposure to HF reduced fruiting of pole bean¹³ and the yield of wheat¹⁴ and snap bean¹⁵ in plants that did not develop leaf symptoms. Disruptions in the processes of pollination or fertilization have been suggested to explain these

observations, but other factors may be involved as well (see below).

The direct effects of fluoride on vegetation are considered to be damaging if the intended use of the plant is impaired. Foliar injuries or growth reductions that do not affect the plant's aesthetic, economic or ecologic value are often of little concern.

INDIRECT EFFECTS ON VEGETATION

Plants as Vectors

Vegetation can serve as a vector for the transfer of fluoride from the atmosphere to other components of an ecosystem. Much of the fluoride accumulated in leaves subsequently enters the upper horizons of soil through litter decomposition. Foliar fluoride may also be transported to insects, livestock and other herbivores. Forage crops are of particular concern. The concentration of fluoride both on and in plant tissues can be important even when there are no effects on the plant *per se*. Consumption of forages by livestock containing elevated concentrations of fluoride may cause dental fluorosis or osteofluorosis.³

Insects and Diseases

Alterations by fluoride of plant-insect and plant-pathogen relationships are examples of indirect effects that can affect yield or increase the costs of production. Research in these areas is limited, but has revealed a broad range of responses. For example, fluoride has stimulated the development of some diseases of plants and inhibited others through direct effects on the disease organism or indirectly by altering the host plant.¹⁶ The effect of fluoride on plant-insect relationships may be through changes in the nutritive value of plants, modifications of chemical cues insects use to find food, or alterations in plant defense mechanisms against insect attack.¹⁷

Compared to direct effects, relatively little is known about these indirect effects of fluoride. It is likely, however, that they will become more important as the frequency and severity of direct effects diminishes. Attention will then be directed towards the more subtle, indirect effects.

FACTORS THAT MODIFY PLANT RESPONSE

There is a sequence of events that must occur before fluoride effects occur in plants: uptake, translocation, and accumulation to a toxic concentration. Any external or internal factor that affects one or more of these events, directly or indirectly, can determine the kind of response, its magnitude, or even whether or not an effect will occur.

Although these factors are interdependent, they can be separated into three groups: exposure properties, plant characteristics and environmental influences. Exposure properties include the chemical and physical forms of the pollutant, its concentration, the duration of exposure and whether it is continuous or intermittent, and the presence of other air pollutants in the atmosphere with fluoride.¹⁸

The biologic factors include genetic influences on the differential sensitivity of different species or even varieties of the same species. The age of tissues or organs and the developmental stage of the plant when exposed to fluoride are also biologic influences that alter plant responses. Environmental factors such as temperature, relative humidity, rainfall, soil moisture, and the quality or intensity of light exert their influence on the plant which in turn determines the degree of response to fluoride exposures. Examples of altered responses for all of these internal and external factors have been

FUTURE OUTLOOK

Although relatively efficient controls for fluoride emissions to the atmosphere are available and regulatory safeguards are in place at most locations in the US, Canada and western Europe, there are still many uncontrolled or poorly controlled stationary sources, especially in the developing world. International cooperation (and possibly subsidies) will be necessary to resolve this gap and reduce the impact of fluoride-emitting industries on local ecosystems. In those areas where controls are in place emissions have been reduced but not eliminated, and the occurrence and severity of obvious 'typical' fluoride injuries to plants have all but disappeared. As a result, greater attention is currently focused on the subtle or indirect effects that are likely to occur from chronic or intermittent exposures to relatively low concentrations of fluoride in the atmosphere. Future research needs to be directed at identifying those subtle effects and the dose-response relationships required to induce them. Results from these kinds of investigations will be necessary to establish realistic and fair air quality standards or guidelines that will permit industry to coexist with agriculture and forestry.

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BIOGEOCHEMISTRY OF TRACE METALS AT THE
HUBBARD BROOK EXPERIMENTAL FOREST, NH

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The biogeochemical cycles of selected trace metals (Al, Cd, Cu, Fe, Mn, Ni, Pb, Zn) were studied at the Hubbard Brook Experimental Forest, NH. Mass balances and soil solution chemistry showed contrasting patterns of metal behavior. Atmospheric deposition of Cd, Cu and Pb greatly exceeded stream outflow, suggesting that the forest is a sink for these metals. Detailed studies of Pb have indicated that inputs of this metal largely accumulate in the forest floor. Soil solution concentrations of Pb declined with depth in the mineral soil, resulting in low concentrations in streamwater. There was a large net loss of Al and Mn from the ecosystem, indicating that the forest is a source of these elements. Soil solutions also exhibited elevated concentrations of potentially toxic inorganic monomeric Al. Atmospheric inputs of other metals were nearly balanced by outputs (Fe, Ni, Zn). The chemistry and transport of these metals is discussed.

Introduction

There is concern over the effects of atmospheric deposition on the biogeochemistry of trace metals in forest ecosystems. Inputs of acidic atmospheric deposition to acid-sensitive (low base saturation) watersheds may result in the acidification of soil and drainage water^{1,2}. This process can facilitate leaching of trace metals and may have adverse consequences on interconnected aquatic ecosystems^{3,4}. Atmospheric deposition may also serve as an important pathway of trace metal influx to forest ecosystems^{5,6}.

A variety of biotic and abiotic processes can alter trace metal cycling within forest ecosystems. Trace metals can be immobilized within the forest floor by adsorption^{7,8,9}. Conversely, soluble organic acids from leaf leachate or mineralization of soil organic matter may form aqueous complexes with trace metals, facilitating transport to the lower mineral soil or to surface water^{10,11}. The mineral soil may serve as a trace metal sink through adsorption and precipitation reactions or as a trace metal source through desorption and dissolution reactions^{12,13}. Finally, forest vegetation may assimilate trace metals and facilitate cycling through canopy leaching, or decomposition of leaf and root litter^{5,15,16}.

Mass balances are an effective tool in understanding the transport of trace metals to and within forest ecosystems, and their effects on surface waters. The Hubbard Brook Experimental Forest in New Hampshire has been a site of element cycling studies since 1963. By monitoring precipitation inputs and stream outputs from small watersheds that are essentially free of deep seepage, it is possible to construct accurate element balances. The precipitation and stream monitoring program at Hubbard Brook has been supplemented by detailed studies of soil and soil solution chemistry, and forest floor and vegetation dynamics. The objective in this study was to compile and summarize available information on the biogeochemistry of selected trace metals for the Hubbard Brook Experimental Forest.

Experimental Methods

Study Site

The Hubbard Brook Experimental Forest (HBEF) is located in the White Mountains of New Hampshire (43°56'N, 71°45'W). This investigation was conducted in watershed 6 (w6), the biogeochemical reference watershed at Hubbard Brook (13.23 ha, elevation 546-791 m; Figure 1). The watershed has a southeasterly aspect and a slope of 20-30%¹⁶. Soils at the site are acidic, well-drained Spodosols (Haplorthods and Fragiorthods) with a well drained organic layer (3-15 cm). They are underlain with variable depths of glacial till and impervious bedrock (Littleton formation; schist)¹⁶. Soils are shallow at high elevations and increase in depth with decreasing elevation¹⁷.

Climate at the HBEF is cool temperate, humid continental with mean July and January temperatures of 19°C and -9°C, respectively (at 450 m elevation). Mean annual precipitation is approximately 130 cm, with 25-33% of the total occurring as snow^{15,16}. Mean annual streamflow from w6 is 80 cm¹⁶.

Northern hardwood vegetation dominates most of w6, consisting of American beech (Fagus grandifolia Ehrh.), yellow birch (Betula alleghaniensis Britt.) and sugar maple (Acer saccharum Marsh.), from 500-730 m. Coniferous vegetation, consisting primarily of red spruce (Picea rubens Sarg.) and balsam fir (Abies balsamea (L.) Mill) dominates elevations above 730 m. The HBEF was logged between 1909-1917, and there is no evidence of recent fire¹⁵.

Data Analysis

This paper is a summary of many trace metal studies that have been conducted at the HBEF. Data collected include fluxes and concentrations of trace metals in bulk precipitation, streams^{18,19}, soil solutions^{13,20}, forest floor^{18,21}, mineral soil²¹ and vegetation¹⁵. Details of sampling and analytical methods for these studies are provided elsewhere. Trace metal biogeochemistry from these studies are summarized here through element budgets (Figure 2). Ecosystem element pools include: above and below ground biomass, the total forest floor content, exchangeable metals in E+Bh horizons, Bs1 horizon and Bs2 horizon soil, and the total mineral soil pool (< 2mm size fraction). Ecosystem fluxes include bulk precipitation inputs, uptake by biomass, solution fluxes through the Oa, Bh and Bs horizons and stream outflow. Weathering fluxes are not determined directly but are calculated as differences in the mass balance. This calculation assumes that exchangeable element pools are at steady-state.

Results and Discussion

Element balances for the trace metals studied show distinct patterns (Table 1). Values of atmospheric deposition of trace metals at Hubbard Brook are high for a remote area, but are consistent with other studies of trace metal deposition in the northeastern United States^{5,6,22}. Streamwater outputs are dominated by dissolved or fine particulate forms. This pattern is consistent with the low sediment transport from this undisturbed forest. Exceptions to this are evident for Al and Fe. These metals show 41% and 30% of their efflux associated with particulate matter. Mass balance calculations show three general classes of trace metals: 1) metals that are strongly retained within the ecosystem (Cd, Cu, Pb); 2) metals that are strongly leached from the ecosystem (Al, Mn); and 3) metals that approximately balance between atmospheric deposition and stream losses (Fe, Ni, Zn). To illustrate differences in trace metal chemistry we present detailed budgets for Pb and Al.

Lead Budget for the HBEF

Smith and Siccama¹⁸ previously developed a Pb budget for Hubbard Brook. With additional data on soil²¹ and soil solution¹³ chemistry we are able to expand this budget (Figure 3a). Atmospheric deposition of Pb has been declining since Pb was added to the precipitation monitoring program in 1975^{18,19}. This decline is consistent with the decreased use of leaded gasoline over the same period^{19,23}.

The mineral soil and forest floor are the major pools of Pb in the ecosystem (Figure 3a). Mineral soil pools are generally the largest element pools for the HBEF¹⁶, however this includes relatively unreactive soil minerals. Deposition and accumulation of Pb in the forest floor has been the focus of a number of investigations^{6,9,18,22}. At Hubbard Brook much of the Pb entering the ecosystem from the atmosphere appears to be retained in the forest floor. Concentrations and fluxes of Pb in bulk

precipitation are much greater than in Oa horizon leachate. Concentrations and fluxes of Pb decrease through the soil profile¹³ and losses in streamwater are low. Driscoll et al.¹³ noted that there was a strong correlation between concentrations of Pb and dissolved organic carbon (DOC) in soil solutions and streamwater at Hubbard Brook. Moreover Smith and Siccama¹⁸ showed that acid extractable Pb concentrations were elevated in the forest floor (0.43 mmol/kg), low in the E horizon (0.025 mmol/kg), intermediate in the B horizon (0.058 mmol/kg) and low in the C horizon (0.042 mmol/kg). This pattern is consistent with decomposition and release of DOC from the forest floor, transport through the E horizon and deposition in the B horizon which occurs as part of soil development (the podzolization process). Mobilization and immobilization of Pb at Hubbard Brook appears to be associated with the dynamics of soil organic matter.

Vegetation pools and uptake of Pb at Hubbard Brook are small. Lead is not a plant nutrient²⁴ and therefore it is not surprising that assimilation is low. The calculated weathering input for Pb at Hubbard Brook is negative (-0.84 mol/ha-yr). This is likely due to changes in mineral soil Pb pools over the study period. Siccama²⁵ has observed marked declines in the Pb content of the forest floor. This pattern is probably due to the recent decreases in precipitation inputs of Pb.

There has been some concern over the effects of elevated inputs of Pb to forest ecosystems^{5,6,9,18}. These potential effects include leaching of Pb to surface waters²⁶ and mineralization of Pb in the forest floor and release following clearcutting disturbance¹⁸. Results from long-term monitoring at Hubbard Brook suggests that streamwater concentrations are very low and not a water quality concern^{13,18}. In addition, a study of Pb in soil solutions and streamwater following a commercial whole-tree harvest at Hubbard Brook showed that Pb was not released to drainage waters from clearcutting activities²⁷.

Aluminum Budget for the HBEF

The Al cycle is characterized by large soil pools and relatively small fluxes (Figure 3b). The Hubbard Brook Al budget shows that the watershed exhibits a large net release of Al, originating from dissolution of soil minerals. Studies from the HBEF have shown that soil and streamwaters are in apparent equilibrium with $\text{Al}(\text{OH})_3$ solubility^{17,28,29}. The solubility of aluminosilicate minerals is pH dependent and leaching of Al is elevated under acidic conditions^{1,2}. At Hubbard Brook drainage waters are acidic (pH < 5.0) due to elevated inputs of SO_4^{2-} and limited release of basic cations (Ca^{2+} , Mg^{2+} , Na^+ , K^+). As a result leaching losses of Al are high relative to watersheds which are not impacted by strong acid inputs³⁰.

An understanding of the biogeochemistry of Al at Hubbard Brook has been facilitated by examination of the speciation of aqueous Al. Solution Al is present as nonlabile monomeric Al, which is an estimate of aluminorganic complexes, and labile monomeric Al, which represents inorganic species of Al. The fractionation of Al can be used to assess the cycling of Al in forest soils as well as the potential ecological effects of elevated Al concentrations. Inorganic forms of Al are thought to be toxic to vegetation³¹ and aquatic organisms³². The speciation of monomeric Al in soil solutions draining three horizons (Oa, Bh, Bs) in three elevational zones (spruce-fir, 750 m; high elevation hardwood, 730 m; low elevation hardwood, 600 m; Figure 1) is shown in Figure 4. Organic horizon (Oa) leachate (which is characterized by elevated concentrations of DOC¹³) has high concentrations of Al which is largely in an organic form. Deeper in

the mineral soil, DOC concentrations decrease and Al shifts from predominantly an organic form to an inorganic form. Aluminum losses are most pronounced at high elevation sites with shallow acidic soils. At lower elevations the thickness and base saturation of the mineral soil increases, which coincides with higher soil solution pH and lower concentrations of solution Al.

There is concern over the ecological effects of elevated concentrations of inorganic monomeric Al. For example, surface water concentrations in excess of 7 $\mu\text{mol/L}$ are thought to be toxic to fish³³. Also, high concentrations of Al are thought to contribute to red spruce decline in the northeastern U.S.³⁴ Laboratory experiments suggest that 100 $\mu\text{mol/L}$ inorganic monomeric Al is a toxic threshold for red spruce³⁵. In addition, laboratory experiments have indicated that an Al/Ca molar ratio above 1 may impair red spruce growth³⁶. Soil solutions from the spruce fir zone at Hubbard Brook are well below the concentration threshold (average inorganic monomeric Al concentrations were 1 $\mu\text{mol/L}$ in Oa soil solutions and 22 $\mu\text{mol/L}$ in Bs soil solutions). The Al/Ca in Oa horizon solutions (0.04) is well below the critical value of 1, however the Al/Ca in the Bs horizon (1.6) is somewhat above this level. While there is no evidence of spruce decline at Hubbard Brook, the effects of elevated concentrations of Al warrant further study.

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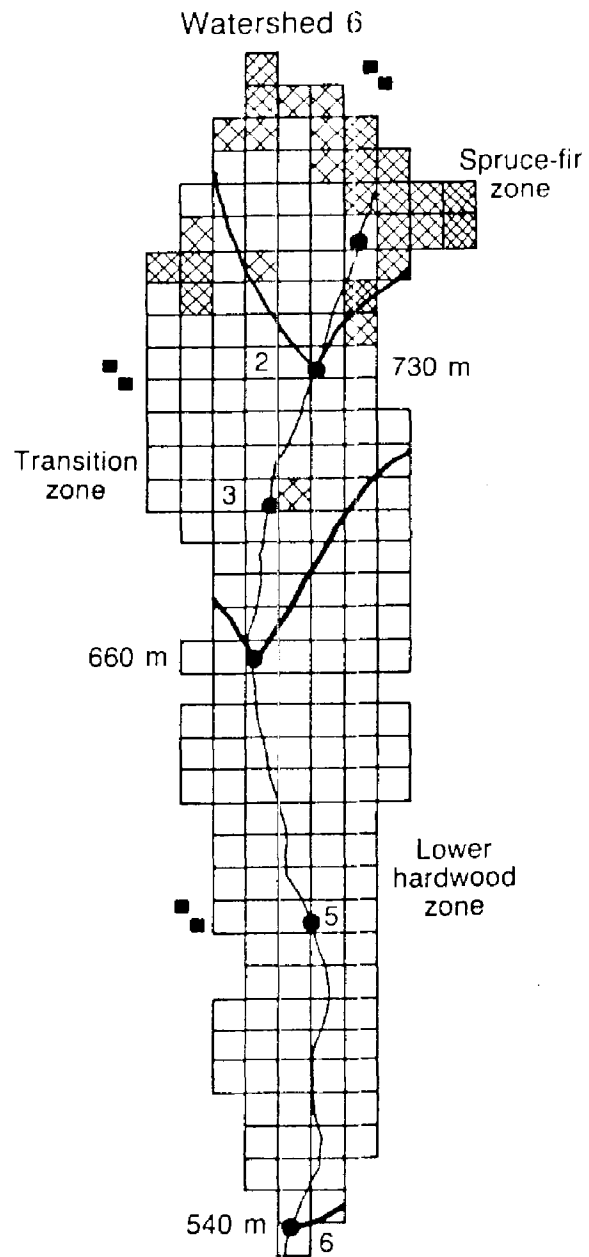
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Table 1. Trace Metal Input/Output Budgets for w6 at the HBEF (mol/ha-yr)

	Input	dissolved	Output particulate	Net
Aluminum (Al)	8	74	51	-117
Cadmium (Cd)	0.11	0.013	9×10^{-5}	+0.099
Copper (Cu)	0.25	0.077	0.003	+0.17
Iron (Fe)	8.3	7.3	3.2	-2.2
Lead (Pb)	0.92	0.021	0.004	+0.89
Manganese (Mn)	1.8	8.2	0.12	-6.6
Nickel (Ni)	0.24	.17	0.003	+0.07
Zinc (Zn)	2.1	2.2	0.02	-0.1



Percent basal area (m^2/ha)
of spruce plus fir trees

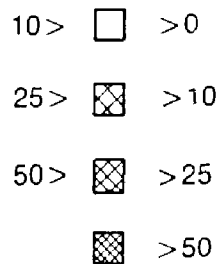


Figure 1. Map of HBEF watershed 6. Lysimeter and stream sampling stations are indicated. The percent basal area of red spruce and balsam fir vegetation are shown.

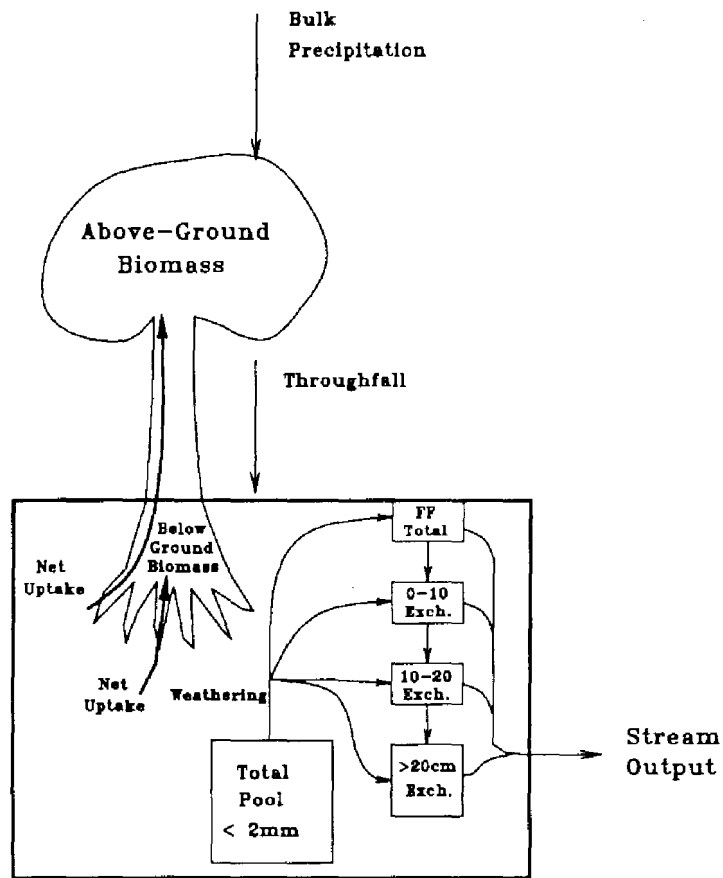


Figure 2. Schematic drawing of the biogeochemical cycle in a forest ecosystem.

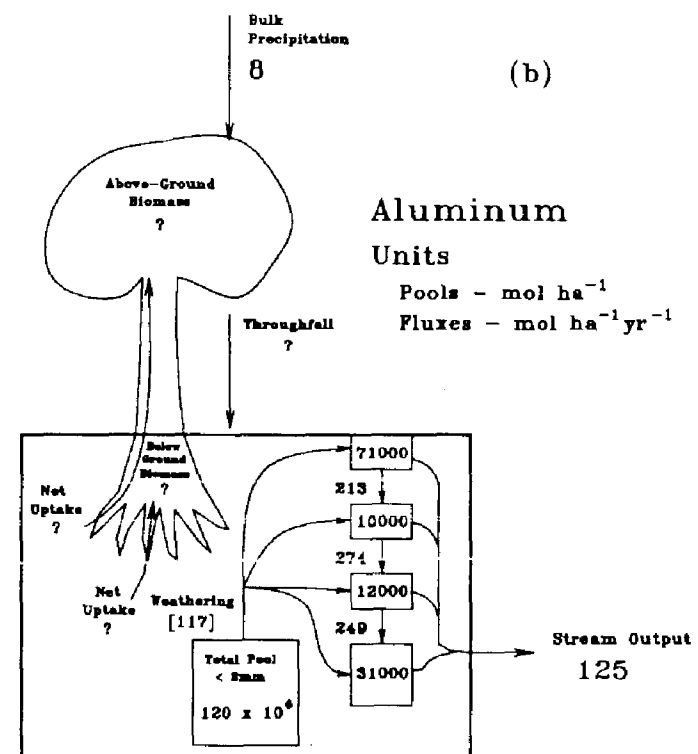
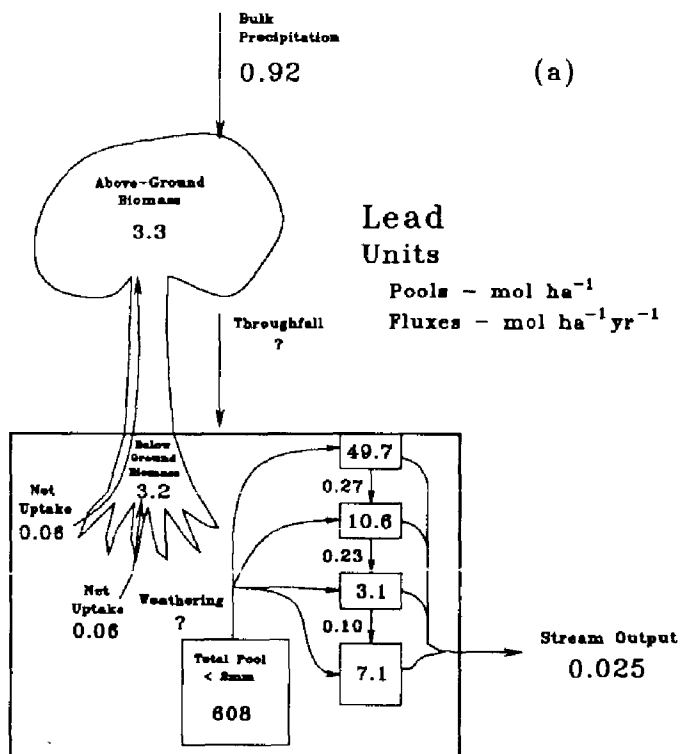


Figure 3. Biogeochemical cycles of Pb (a) and Al (b) at Hubbard Brook.

Monomeric Al Fractionation

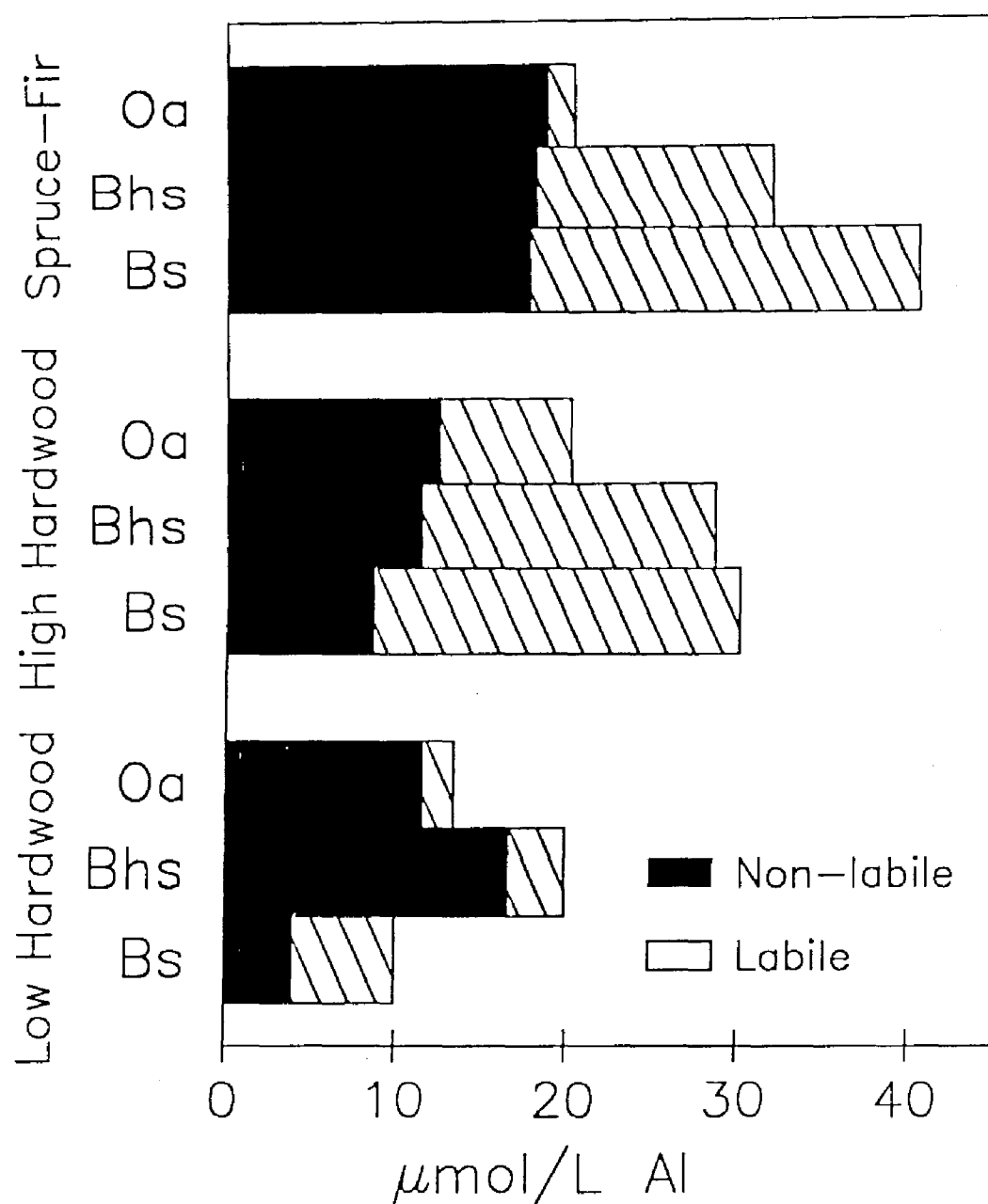


Figure 4. Concentrations of nonlabile (organic) and labile (inorganic) monomeric Al in soil solutions draining Oa, Bh, and Bs horizons at three vegetation zones. The lysimeter sampling stations are shown in Figure 1.

USE OF THE PHYTOTOX DATABASE TO ESTIMATE THE INFLUENCE OF HERBICIDE DRIFT ON NATURAL HABITATS IN AGROECOSYSTEMS

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It was shown that if the maximum amounts of trifluralin and alachlor known to volatilize from plowed fields are assumed to be wind blown onto adjacent vegetation in an oak-hickory plant community the growth of 8 different genera could be influenced. The most sensitive plant genera were *Urtica* and *Cassia*. The PHYTOTOX database provides a tool for estimating the influence of herbicide drift on the productivity and composition of natural plant communities.

Introduction

In agroecosystems, there exists a patchwork of row crops intermixed with pasture and natural plant communities. The extensive use of herbicides in various agroecosystems across the U.S. poses a potential threat to vegetation growing on adjacent land if chemicals applied to cropland inadvertently drift onto nontarget areas. Adverse consequences of such an event could be: reduced production of plant biomass (yield), and/or change in the species composition (diversity) of the nontarget plant community. Whether or not a plant community is effected in either or both of these ways is dependent on two factors: the nature of the exposure and the sensitivities of the plant species within the nontarget community.

Estimating chemical exposure of nontarget plants depends on several variables: the chemical gradient (concentration vs. distance) extending across the nontarget zone, duration of exposure, and frequency of exposure. The magnitude of each of these variables depends in turn on the chemical and physical properties of the compound, mode of application, and prevailing weather conditions. Since all of these parameters can be quantified the process of predicting the amount of drift and subsequent exposure of nontarget vegetation lends itself to mathematical modeling. A variety of distinctive models have been developed by various investigators to deal with different combinations of pesticide application (plane vs. tractor), chemical features (liquid vs. dust), and mode of drift (direct from applicator or indirect following volatilization from field).

The response of nontarget vegetation to pesticide drift has received less attention than development of the drift models. Some models appear to have never been validated by biomonitoring¹, and others have only been validated by examining cultivated crops². There are only a few isolated reports on how herbicides influenced the productivity or composition of native plant communities^{3,4,5,6,7}. Only one of the reports was done in connection with drift modeling, one dealt with a tree community, and none considered the influence of indirect (field volatilization) drift.

In the absence of such studies, an alternative is to use dose-response data taken from the literature for individual plant species which are known to be present in natural plant communities frequently found in pesticide treated agroecosystems. The dose-response data compiled in the PHYTOTOX database⁸ is ideally suited for predicting potential hazards posed by pesticide drift to nontarget vegetation. In this pilot study we used a portion of PHYTOTOX to predict the potential hazard posed by the volatilization and drift of trifluralin and alachlor on forest communities in Illinois.

Materials and Methods

The PHYTOTOX database is a computerized information resource that permits the rapid retrieval and comparison of data pertaining to the response of terrestrial plants to the application of organic chemicals⁸. As of January 1, 1990, PHYTOTOX possessed information on approximately 8,000 different chemicals, 2,000 species, and 50 plant responses. The data has been compiled from over 3,500 articles published between 1926 to 1988. The database has two files: a Bibliographic File and an Effects File. The Bibliographic File possesses information on each paper which has been used as a source of data for compiling effects records. The Effects File contains approximately 100,000 records. The Effects File differs from most biological databases, because it contains quantitative numerical data pertaining to chemical doses, plant responses and experimental parameters. Each record in the Effects File contains information concerning the effect(s) of one dose of a single chemical

applied to a particular plant species as reported in one publication. The information associated with each record is organized under labels that may be sorted separately during computer searches.

Trifluralin and alachlor were examined in this study, because of their high usage on corn and soybeans in Illinois⁹, and their strong tendency to volatilize from the soil^{10,11}. Attention was focused on the oak-hickory community since small wood lots meeting this description are interdispersed among corn and soybean fields in Illinois¹². A hierarchical search of PHYTOTOX was conducted to recover data pertaining to oak-hickory community plants treated with comparative doses (kg/ha) of either trifluralin or alachlor.

Results

PHYTOTOX possessed information on 100 species which occur in oak-hickory communities. This number was reduced to 8 when only records pertaining to trifluralin and alachlor were considered (Table I). The plant list was expanded to include data on an additional 10 species which are in the same genera as plants found in oak-hickory communities. Justification for expanding the list in this manner comes from previous analyses where it was shown that species within the same genus had a high correlation of response to the same chemical¹³.

Examination of the data in Table I shows that different species vary widely in their sensitivities, and a single species will respond differently to different herbicides. For example, while Senecio vulgaris experienced 100% control (kill) when treated with 1.9 kg/ha alachlor, it was not affected at all by a somewhat lower dose of trifluralin. This variable response by different plant species to chemicals has been capitalized on in selectively killing unwanted plants in cultivated fields. This feature also has the potential of eliminating biodiversity in nontarget areas if the amounts of drifting chemicals reach the inhibitory level for sensitive plants.

Trifluralin is an extremely volatile herbicide. Glotfelty et al. have shown that 90% of the trifluralin applied to moist soil will be lost to the air in 2-7 days following application¹⁰. These investigators established the maximum rate of volatilization to be 195 g/ha/h and measured air concentrations as high as 40 $\mu\text{g}/\text{m}^3$ (0.003 ppm) at 50 cm above the soil surface. Based on these data it can be hypothesized that if 2.8 kg/ha is applied to a cultivated field it is possible that moving air could transport 2.5 kg/ha to adjacent nontarget plants over a 2-7 day period. When this level of exposure is compared to dose-response data in Table I it was found that 8 different genera (Acer, Cassia, Dioscorea, Ilex, Rhododendron, Solanum, Thuja, and Urtica) had sensitivities low enough to be affected. Among these genera the species Urtica chamaedryoides is on the Illinois endangered and threatened species list.

Alachlor has a lower field volatility than Trifluralin, but even at the reduced rate of 8.1 g/ha/h it has been shown that 19% of applied doses (420 g/ha) were lost in 21 days¹¹. If weather conditions caused this amount of volatilized alachlor to be redeposited on vegetation adjacent to an applied field it could influence the growth of 3 genera listed in Table I. This level of alachlor exposure represents 25% of a dose giving 23% control (kill) of Cassia obtusifolia and 22% of a dose giving 100% control of Urtica urens and Senecio vulgaris (Table I). Two species of Cassia, 3 of Senecio, and the aforementioned U. chamaedryoides growing in Illinois woodlots could be affected.

Conclusions

A comparison between maximum drift values estimated from the literature with dose-response data taken from PHYTOTOX indicated that some nontarget species growing in oak-hickory communities could be influenced by the drift of trifluralin and/or alachlor. The most sensitive plants were Cassia and Urtica. Although we are not aware of any field measurements or biomonitoring data collected in native plant communities which would substantiate this prediction, there is a report by Behrens and Lueschen where 0.28 kg/ha of dicamba applied to a corn field affected soybean growth 60 m downwind in an adjacent field¹⁴. Such data certainly is cause for concern and suggests that herbicide drift may have a profound influence on the productivity and composition of natural plant communities.

The biota of the U.S. has been described as having approximately 116 different native plant communities¹². The geographical location and species composition of each of these communities is known. Therefore it is possible to identify natural plant communities which are in association with various crops in different agroecosystems located throughout the U.S. In this pilot study with PHYTOTOX we considered only one plant community (the oak-hickory forest) and only two herbicides (trifluralin and alachlor). Similar analyses could be conducted for all 116 plant communities in the U.S. and for an extended list of herbicides.

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Table I. Dose-response data from PHYTOTOX for two herbicides commonly used in Illinois and taxa from genera known to occur in Illinois wood lots.

Plant		Herbicide			
		Trifluralin		Alachlor	
Species	Common Name	Dose kg/ha	Response ^b %	Dose kg/ha	Response ^b %
<i>Acer palmatum</i> ^a	Japanese maple	3.1	20 injury	6.2	Injury
<i>Cassia obtusifolia</i> ^a	Sickle-pod	0.9	81 control	1.7	23 control
<i>Dioscorea</i> sp.	Wild yam	0.2	3 DMD		
<i>Euonymus fortunei</i> ^a	Wintercreeper			20.0	49 DMI
<i>Ilex cornuta</i> ^a	Chinese holly	8.9	16 RT FMD		
<i>Ilex crenata</i> ^a	Japanese holly	2.5	18 LF CHL	12.5	6 SZI
<i>Juniperus horizontalis</i>	Creeping cedar			13.6	None
<i>Pinus echinata</i>	Short-leaf pine	1.1	None		
<i>Pinus strobus</i>	White pine	4.5	None		
<i>Rhododendron obtusum</i> ^a	Kirishima azalea	2.5	35 TRD	6.0	9 injury
<i>Sedum brevifolium</i> ^a	Stonecrop			2.5	15 injury
<i>Senecio vulgaris</i> ^a	Common ragwort	1.1	None	1.9	100 control
<i>Solanum nigrum</i>	Black nightshade	0.6	15 control		
<i>Solanum</i> sp.	Hairy nightshade ^a	0.6	35 control		
<i>Thuja occidentalis</i>	White cedar	0.6	3 TRD	13.6	None
<i>Urtica urens</i> ^a	Burning nettle	2.5	100 kill	1.9	100 control

^aTaxa which do not occur in Illinois woodlots but are members of genera that can be found in Illinois wood lots.

^bAll responses refer to whole plants unless indicated otherwise. Control - similar in meaning to plant kill, DMD - dry mass decrease, DMI-dry mass increase, LF CHL-leaf chlorosis, RT FMD - root fresh mass decrease, SZI-size increase, TRD-transpiration decrease.

DETECTING EFFECTS OF AIR TOXICS USING WILDLIFE

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Biologists and resource managers are interested in the impacts of air toxics on wildlife from two perspectives. First, animals can provide early detection of the presence of air toxics in the ecosystem. Their response can contribute to our knowledge of biological damage and of both human and animal health effects, as well as assist with the establishment of emission standards. Second, effective protection and management of wildlife requires information about any aspect of their environment that can directly or indirectly impact their status and function in the ecosystem. Once an air toxic is detected in a species it must also be interpreted in terms of consequences to the individual (e.g., mortality, reduced vigor), population (e.g., genetic loss), and ecosystem (e.g., change in energy transfer). Information about ecological effects exists for only a small number of the 308 chemicals classified as air toxics. Animals have an important role in the development of the risk assessment methodology associated with airborne contaminants. Many challenges remain in developing effective biomonitoring programs. No standards currently exist for most air toxics and few protocols have been established for standardizing data collection and analyses.

INTRODUCTION

The air resource provides the exchange of gases basic to life. It also serves as the pathway and transportation medium for a diversity of materials, including contaminants. Animals have long served as biological indicators and monitors of harmful chemicals in the air environment^{1,2}. The task of regulating these chemicals and their potential impacts to total ecosystems has been hindered, however, by inadequate development of concepts and methods that translate individual effects to populations and ultimately to the ecosystem level³. Ecosystems may modify the transport, fate, and effect of the chemical (positive/negative interaction) or accumulate and magnify the effects (negative interaction). New ecosystem threats, including global warming, climate change, and increasing levels of volatile organics, offer additional challenges to both detection and measurement of effects. Animals have an important role in the development of associated risk assessment methodology.

Definition of Air Toxics

Air toxics are classified as all non-criteria pollutants as defined by Section 313 of the Superfund Amendments and Reauthorization Act (SARA) of 1986. They include 308 chemicals and 20 chemical categories. The chemicals include a large number of organics (e.g., benzene, ethylene, vinyl chloride) as well as pesticides (e.g., lindane and aldrin, and 2,4-D); inorganics (e.g., nitric acid, sulfuric acid); and metals (e.g., arsenic, mercury, cadmium). The 20 chemical categories are primarily metallic compounds along with PCBs, chlorophenols, and glycol ethers⁴. EPA has published a list of industrial processes and sources that emit air toxics including chemical plants, chrome plating facilities, coal-fired power plants, dry cleaners, and non-point sources such as landfills, mines, and residential wood combustion areas⁵.

Legislation

The laws currently regulating toxic substances include: (1) Clean Air Act (CAA) of 1970, as amended 1977; (2) Federal Water Pollution Control Act (FWPCA) of 1972, as amended 1977 (also known as the Clean Water Act); (3) Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) of 1972, as amended in 1975 and the Federal Pesticide Act of 1978; (4) Safe Drinking Water Act (SDWA) of 1974; (5) Marine Protection Research and Sanctuaries Act of 1972 (Ocean Dumping Act); (6) Resource Conservation and Recovery Act of 1976 (RCRA); (7) Toxic Substances Control Act (TSCA) of 1976; and (8) the Comprehensive Environmental Response, Compensation, and Liability Act ("Superfund") of 1980⁶. These laws are designed to safeguard human health and the environment, and animals are an important link in detecting, monitoring, and evaluating impacts.

WILDLIFE AS INDICATORS

Biological Considerations

Biologists and resource managers are interested in the impacts of air toxics on wildlife from two perspectives. First, animals can provide early detection of air toxics in the ecosystem and their response can contribute to our knowledge of health effects and assist with the establishment of emission standards. Wildlife indicators may provide conservative estimates of pollutant effects on human populations. Second, effective protection and management of wildlife requires information on any aspect of their environment that can directly or indirectly impact their status and function in the ecosystem. Air toxics represent one of the major external threats to many of these natural systems⁷. Once an air toxic is detected in a species it must additionally be interpreted in terms of consequences to the individual (e.g., mortality,

reduced vigor), population (e.g., genetic loss), and ecosystem (e.g., change in energy transfer). Wildlife in sub-optimal habitats may be more sensitive to air emissions than portions of the same population in more suitable parts of their habitats. This difference has implications especially for endangered and threatened species that may already be restricted to limited habitats. Federal land managers responsible for wilderness areas and Class I (clean air) lands are particularly interested in developing biomonitoring that can be implemented in remote areas with restricted access and with limitations for collecting air toxics information by conventional methods and equipment⁸.

There is also a need to understand the synergism and antagonism that may exist with air toxics. When one air contaminant is a problem, invariably other contaminants occur with varying and conceivable opposing effects. The toxicity of airborne pollutants is influenced by a number of variables, including type and concentration of pollutant, prevailing winds, temperature, humidity, precipitation, topography, season, species, age, management and activity of animals, length of exposure, nutrition, genetics, and physiology⁹. Toxics that affect a diversity of animals, persist for extended periods in the environment, are mobile, have a high solubility in fat, and have high potential for bioaccumulation are of particular concern.

Unfortunately information about ecological effects exists for only a small number of the 308 chemicals classified as air toxics. Substantial information exists on the ecological effects for most metals classified as air toxics. For some of these metals, such as arsenic, ecological effects have been reported for over 100 years¹. Except for pesticides classified as air toxics, very little information exists on the effect of most organic air toxics on free-living animals.

Wildlife species have good potential as biological indicators of air toxics for several reasons: (1) they integrate all environmental conditions, both natural and man-made, in their responses; (2) they can show pathway points of accumulation and stress in natural and man-influenced ecosystems; and (3) they can be used as biological standards to verify the physical and chemical standards of air quality.

Wildlife may be used to assess air toxics in three main ways. The most commonly used method is to monitor residues or tissue concentrations of chemicals that are not readily metabolized and excreted. This group of compounds includes most metals, fluoride, and lipid soluble organics. Second, sublethal responses of animals to air pollutants may be monitored. This bioindicator approach has been applied frequently in recent years, both for air and other sources of pollutants. Physiological responses, especially enzyme activities, have proven useful for some chemicals¹⁰. However, many physiological responses are not specific for individual chemicals, and hence, is one of the drawbacks of this approach. Despite almost three decades of interest and research in wildlife toxicology, interpretive information for chemical residue data and physiological responses extends to only a few substances, and is further limited by species sensitivities and substrates (bone vs. blood, for example). Therefore, a third approach, assessment of effects on populations (although in reality it is often individuals), is being welcomed into the field. This approach, which generally examines recruitment and survivorship, is the most difficult, but perhaps the most meaningful, for wildlife populations.

The routes of exposure of animals to air toxics can be either direct or indirect. Animals are directly influenced by inhalation of toxic gases, particulates, and aerosols. Indirectly, animals may be affected by ingestion of contaminated food and water. Herbivores are exposed when toxics are accumulated by vegetation from direct deposition on plant surfaces or through the soil. Nutritional value of the vegetation may also be reduced. Carnivores can be similarly affected by consumption of prey species that have bioaccumulated toxics. Indirect effects also include the loss of potential prey and habitat degradation from

the effects of the toxics.

Although animals are routinely used in laboratory testing of new chemicals and to develop standards for human health, extrapolation of laboratory results to natural populations and ecosystems rarely occurs. In the natural environment, communities may be less susceptible than individuals to a particular stress because the more tolerant individuals may replace the most susceptible ones, providing continuity in the community trophic dynamics. Alternatively, communities may be more susceptible than individuals because of the loss of species (or individuals) causing a change in the functioning of the ecosystem, resulting in a pyramid of effects¹¹.

Bioindicator Selection

The use of animals as indicators of air pollutants, including air toxics, has been reviewed in a number of recent reports^{12,13,14}. Factors to be considered in selecting wildlife indicators are trophic level, food habits, sensitivity to chemicals, availability for sampling, population age structure (many substances, cadmium for example, show a strong tendency to accumulate with age), and species mobility (which correlates with time potentially spent in contaminated environments). For situations in which the air toxic accumulates on plant surfaces or is incorporated in plant material, herbivorous animals would be best suited for a monitoring program because larger quantities of an air toxic per unit body weight enter the body via ingestion as compared to inhalation. Capture, collection, and sampling methods are also important. Proper instruments and handling techniques need to be followed to avoid contamination of samples after they are collected.

DISCUSSION

Many challenges remain in developing effective wildlife biomonitoring programs. No standards exist for most of the air toxics and there is a critical need for information about biological and ecological effects. There is a general lack of ambient data and few protocols have been established for standardizing data collection and analyses.

The ecological impact of atmospheric pollutants emitted from point-sources depends upon both meteorological and biological factors. Modeling may provide some help in assessing and interpreting these interactions. Dixon and Murphy proposed a discrete-event approach to predicting the effects of atmospheric pollutants on wildlife populations¹⁵. This approach provides recurrent exposure to short-term pulses of high concentration and can be correlated to seasonal variation in biological activity. Initial results of this type of model suggest that the biological response to varying concentrations of pollutants may differ from responses to chronic low-level exposures. Further work in this area is needed.

National biomonitoring programs have been used to some extent and new initiatives are underway. The National Contaminant Biomonitoring Program has produced some broadly-scoped information on the relations between biological populations and certain environmental contaminants¹⁶. This program is currently restricted to collecting information on persistent organochlorines and some inorganic contaminants including arsenic, cadmium, copper, lead, mercury, selenium, and zinc. The Environmental Monitoring and Assessment Program (EMAP) proposed by the Environmental Protection Agency will establish standard procedures and an interagency network of ecological monitoring for a variety of materials (D. McKenzie, pers. comm.). Efforts are also underway by the Fish and Wildlife Service to develop a National Wildlife Refuge Monitoring Program focused on contaminants and wildlife. These types of efforts will be further assisted by research conducted by facilities such as the Institute of

Wildlife and Environmental Toxicology, which studies the use of chemicals as they affect wildlife¹⁰.

Ecotoxicology is the emerging multidisciplinary field of science that mixes toxicology, which is concerned with effects at the level of the individual organisms, with environmental chemistry, which measures occurrence of chemicals in the environment and analyzes processes related to their distribution, and with ecology, which deals with the relations among species and their abiotic environment¹⁷. Wildlife, as indicators and monitors, have an important function in the linkage of these fields.

As new approaches are developed for detecting and monitoring air toxics, continuing attention should be given to those wildlife species that best serve as biological filters for selected toxics and for those sensitive species that occupy key positions in regulating important ecosystem functions.

ACKNOWLEDGMENTS

We thank Jim Fleming for his comments and input on discussions on this topic and Rita Villella, David Lemarie and Judy Scherpetz for their reviews of early drafts.

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EFFECTS OF AIR POLLUTANTS ON COLD-DESERT CYANOBACTERIAL-LICHEN
CRUSTS AND ROCK LICHENS: CHLOROPHYLL DEGRADATION, ELECTROLYTE
LEAKAGE AND NITROGENASE ACTIVITY

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Exposure of cold-desert cyanobacterial-lichen crusts on three different substrates (sandstone, limestone and gypsum) to different pollution sources showed that while urban pollutants in the Los Angeles basin, especially particulates, significantly degraded chlorophyll on all three substrates, simulated acid rain (pH 3.5, 4.5, 5.5 and 6.5; 1:1 sulfuric and nitric acid) had an opposite, fertilizing effect on sandstone and limestone crusts. Studies around a coal-fired power plant, comparing sites 9 and 12 km away from the plant with a control site 42 km away, showed the same fertilizing effect on surrounding sandstone crusts. However, less pH-buffered rock lichens had significantly increased electrolyte leakage and chlorophyll degradation at the nearer sites; nitrogenase activity in a crustal soil lichen was depressed as well. When exposed to power plant effluents or simulated acid rain, the degree of contact with the pH-buffering substrate was important: cyanobacteria, embedded in soils that buffered acidity, may use nitrates and sulfates as fertilizers. Rock and soil lichens, with less contact and less buffering, showed opposite effects. Chlorophyll degradation in crusts by urban pollutants, especially particulates, suggests that pollutants other than acid-producing or gaseous ones injure crusts as well. Combined, these data suggest that the deleterious effects seen in this study from power plant emissions and simulated acid rain are caused by different agents than those injuries due to urban pollutants.

Introduction

Many studies have demonstrated the usefulness of non-vascular plants for biomonitoring of air pollutants in humid environments. Much less work has been done on species located in semi-arid or arid regions. This study examined the effects of different types of air pollutants on cold desert cyanobacterial-lichen soil crusts and rock lichens from the Colorado Plateau, using chlorophyll degradation, electrolyte leakage and nitrogenase activity as indicators of stress. Study sites included a coal-fired power plant, dry deposition chambers in the Los Angeles Basin, California, and wet deposition chambers in Riverside, California.

Methods

The rock lichens Rhizoplaca melanophthalma, Lecanora argopholis and Xanthoparmelia taractica, a soil lichen, Collema tenax, and cyanobacterial crusts dominated by Microcoleus vaginatus and Scytonema sp. were used for this study. Samples around the power plant were collected along a transect running north-northeast from the Navajo Generating Station, with study plots located at increasing distances from the plant (6, 12, 21, and 42 km). Plots were located within 150 m of the shores of Lake Powell, and were accessed by boat. All plots were located on Navajo sandstone, at approximately the same elevation (1200 m) and the same exposures (north-northeast to north for rock lichens, flat areas for cyanobacterial crusts and soil lichens). Ten to 20 samples of each species was collected at each site. Samples used in the dry and wet fumigation studies were collected from Canyonlands National Park (sandstone-derived soils), Arches N.P. (gypsiferous soils) and Bryce Canyon N.P. (limestone-derived soils).

Chlorophyll measurements were made using techniques outlined in Ronen and Galun¹. Absorption spectrums were measured in a Hewlett-Packard diode array spectrophotometer. Optical densities used for measurements were determined by scanning between 700 and 400 nm both non-acidified and acidified (using 1N HCl) extracts. Peaks were found at OD435 (chlorophyll a) and OD415 (phaeophytin) for rock lichens; extracts of the cyanobacterial soil crusts showed peaks at OD398 (chlorophyll a) and OD362 (phaeophytin). Results were analyzed using analysis of variance (ANOVA) and Duncan's multiple range test.

For nitrogenase activity, samples of the soil lichen Collema tenax were incubated for 4 hours at 26 C in 2.5 cm diameter, clear, gas-tight tubes with a 10% acetylene atmosphere. Incubation was in a chamber lighted with Chromo50 (5000 K) and cool white fluorescent bulbs; samples were analyzed on a Carle FID gas chromatography equipped with a 8 foot, 8% NaCl on alumina

column, using helium as carrier gas (30 ml/min). Injections were .25 ml. Replicates were generally 10 per site.

Electrolyte leakage (membrane permeability) of the lichen thalli was determined by methods outlined by Pearson². Lichen thalli analyzed were selected for similarity of surface area. Thalli were humidified for 2 hours, rinsed for 3 seconds, and then submersed in deionized water for 5 minutes. Conductivity of the water was measured before and after immersion of the thalli with a Fisher Scientific Conductivity Meter. Thalli were then dried and weighed.

Results

Effects of Power Plant Emissions

The Navajo Generating Station is a coal-fired power plant located near Page, Arizona, that is surrounded by a calcium carbonate-rich sandy substrate. Effects of the plant on both cyanobacterial crusts and rock lichens in the vicinity were evaluated. Samples were collected at distances of 6, 12, 21 and 42 km from the plant. Chlorophyll degradation and electrolyte leakage were measured in rock lichens, while chlorophyll degradation and nitrogenase activity were measured for the soil crusts. Results for the rock lichens (Figure 1) showed greatest chlorophyll degradation in Leconora argopholis at the 12 km site; values were significantly different from those at the 6 and 42 km sites. For Xanthoparmelia taractica, greater degradation was measured at site 12 as well, but the differences could not be shown to be statistically significant. Rhizoplaca melanophthalma showed significantly more chlorophyll degradation at the 6 and 12 km stations than at the 21 and 42 km sites. Rhizoplaca also showed significantly increased electrolyte leakage at the two nearer sites when compared to the two more distant sites (Figure 2).

The pattern of chlorophyll degradation in the cyanobacterial crusts (dominated by Microcoleus vaginatus) near the power plant was opposite that observed for rock lichens (Figure 3). There was significantly less chlorophyll degradation at 12 km than at the 6, 21, or 42 km sites on three of four sampling dates. On the fourth sampling date, there was significantly less degradation at the 21 km site. Chlorophyll degradation levels for the soil lichen Collema tenax did not differ significantly among the sites.

Nitrogenase activity was measured for Collema tenax in 1988, 1989, and 1990 (Figure 4). At all sample dates, nitrogenase activity was depressed at sites 6, 9, 12 and 21 km from the plant relative to control sites at 42 and 225 km from the plant. When the 6, 9, 12 and 21 km sites were combined to make a basin average for the area surrounding the power plant, that mean was

statistically lower than that for the control site on four of the five sampling dates.

Effects of Urban Air: Dry Deposition

Cyanobacterial-lichen soil crusts on soils derived from three different substrates (sandstone, limestone and gypsum) and a rock lichen, Dermatocarpon moulinii, were exposed to urban pollutants in the Los Angeles Basin using dry deposition chambers (Figure 5). In 1988, an eight week exposure resulted in significantly greater degradation of chlorophyll in crusts from limestone and sandstone-derived soils, relative to controls in filtered air chambers. Chlorophyll levels in mosses from all three soils was unaffected by dry deposition, while the rock lichen and crusts from gypsum soils showed significantly more chlorophyll in the unfiltered chambers. Crusts in which chlorophyll was degraded were dominated by cyanobacteria, while the gypsiferous crust was dominated by lichens with green algal phycobionts. The rock lichen tested also had green algal phycobionts. The data suggest that green algae may be more resistant to chlorophyll degradation from urban air pollutants than are cyanobacteria. These observations were supported by the 1989 exposure of these organisms. In those trials, all crusts were cyanobacteria-dominated, including the gypsiferous crust, and all showed significant degradation of chlorophyll.

Effects of Wet Deposition

Cyanobacterial soil crusts were exposed to wet deposition as well (Figure 6). Simulated acid rain (pH 3.5, 4.5, 5.5 and 6.5; 1:1 sulfuric and nitric acid) resulted in a negative correlation between chlorophyll levels and pH (i.e. chlorophyll increased as pH decreased) in crusts from limestone and sandstone derived soils dominated by the cyanobacteria Microcoleus vaginatus. This difference was statistically significant for the sandstone soil crusts although statistical difference could not be shown for the limestone. Sandstone soil crusts with high levels of another cyanobacterial species, Scytonema sp., showed no significant effects. Gypsiferous soil crusts showed increases in chlorophyll from pH 6.5 to pH 4.5, but crusts exposed to rain of pH 3.5 showed a decrease in chlorophyll ($p < 0.07$).

Conclusions

The data suggest that the effects of power plant effluents and simulated acid rain are strongly modified by the degree to which organisms are intermingled with their pH-buffering substrate. Cyanobacteria, embedded in soils that buffer acidity, may use nitrates and sulfates washed out of the atmosphere as fertilizers. Rock and soil lichens that have less contact with the substrate are apparently less buffered and show opposite effects, including significantly increased electrolyte leakage,

increased chlorophyll degradation and decreased nitrogenase activity. Chlorophyll degradation in soil crusts exposed to urban pollutants, especially urban particulates, suggests that pollutants other than acid-producing effluents injure crusts as well. Combined, these data suggest that the deleterious effects seen in this study from power plant emissions and simulated acid rain are caused by different agents than those that cause injuries in urban air. Finally, cyanobacteria may be more susceptible to injury from urban sources than green algae.

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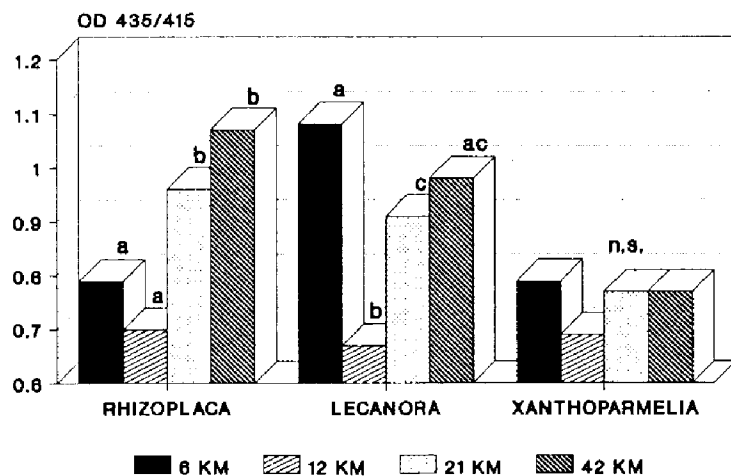


Figure 1. Chlorophyll degradation ratios in three rock lichens near the Navajo Generating Station in Page, AZ (expressed by the spectrophotometric optical densities of 435/415, equal to chlorophyll *a*/phaeophytin). Letters a, b differ at $p < 0.05$.

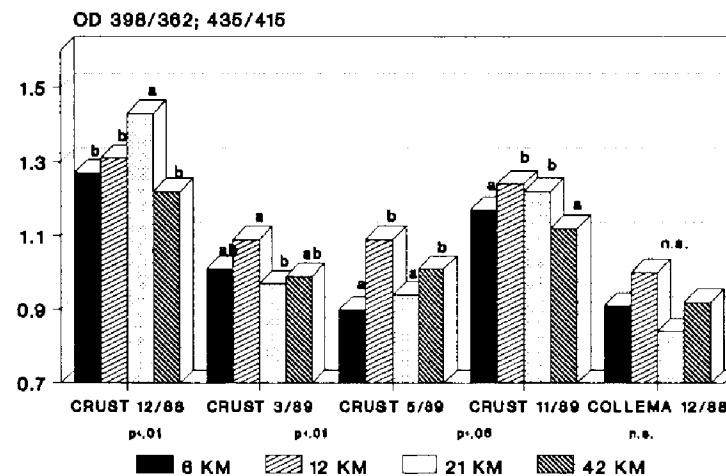


Figure 2. Chlorophyll degradation ratios in cyanobacterial crusts and the soil lichen *Collema tenax* near the Navajo Generating Station in Page, AZ. Letters a, b differ at $p < 0.05$.

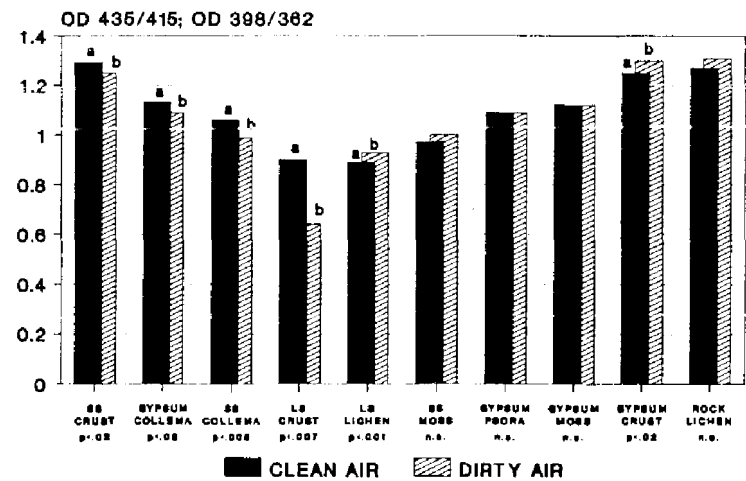
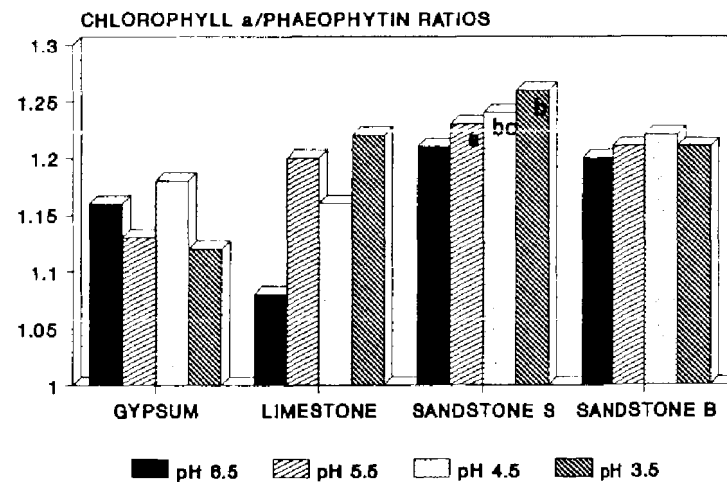
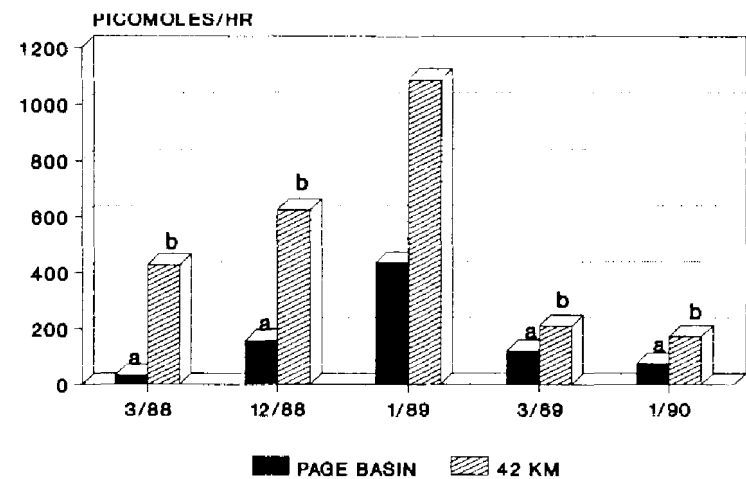
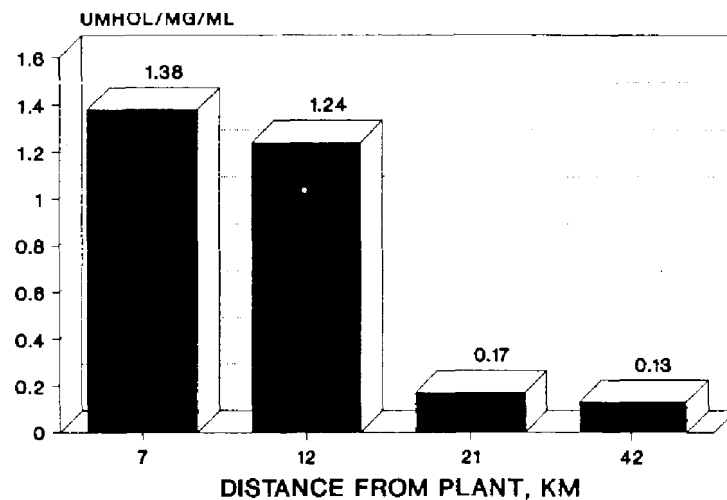


Figure 3-6: Electrolyte leakage in the rock lichen *Rhizoplaca melanophthalma* at different distances from the Navajo Generating Station. Letters a, b differ at $p < 0.01$. 4. Nitrogenase activity in the Page basin (combination of sites 6, 9, 12, and 21 km from the plant) that surrounds the power plant, compared to a control site 42 km away. Letters a, b differ at $p < 0.02$. 5. Soil crusts on three different substrates exposed to dry deposition in the San Bernardino Mountains, California. Letters a, b differ at $p < 0.05$. 6. Soil crusts on three different substrates exposed to wet deposition (1:1 sulfuric and nitric acid) at pH 3.5, 4.5, 5.5, and 6.5. Letters a, b differ at $p < 0.05$.

EVALUATION OF A DIFFERENTIAL OPTICAL ABSORPTION
SPECTROMETER AS AN AIR QUALITY MONITOR

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Abstract

Differential optical absorption spectrometer (DOAS) has been used by a number of investigators over the past 10 years to measure a wide range of gaseous air pollutants. Recently OPSIS AB, Lund, Sweden has developed and made commercially available a DOAS instrument which has a number of features which make the unit attractive for field monitoring studies in remote and urban areas. The DOAS is composed of a broadband light source (emission between 200-1000 nm) and a receiver-spectrometer assembly. The spectral signals from the spectrometer are processed in real time using a personal computer to calculate the concentrations of the pollutants programmed to be monitored by the system. The distance between the light source and receiver can range from 100 m to 2,000 m depending on the pollutant to be monitored and species concentrations. In September and October 1989 an OPSIS AB DOAS was operated in the Research Triangle Park, NC on the roofs of the two main EPA laboratories. The distance between the light source and receiver was 557 m and the pollutants monitored were SO₂, NO₂, O₃, HCHO and HNO₂. Comparisons between the Federal Reference and Equivalent Methods measuring SO₂, O₃ and NO₂ and simultaneous data derived from the DOAS showed excellent agreement with correlations typically greater than 0.90.

Introduction

Since 1979 several studies^{1,2} have been published describing the application of Differential Optical Absorption Spectrometer (DOAS) to measure over long paths, ambient concentrations of nitrous acid (HNO_2), ozone (O_3), sulfur dioxide (SO_2), nitrogen dioxide (NO_2), formaldehyde (HCHO), and nitrate radical (NO_3). Recently a commercial version of the DOAS system has been made available by OPSIS AB, Lund, Sweden.³ This OPSIS (DOAS) is composed of a 150 watt high pressure xenon lamp assembly, optical light receiver, fiber optic cable, spectrometer and personal computer (PC). The spectrometer and software signal processing system rapidly converts UV-visible light intensity signals at 10-60 second intervals into $\mu\text{g}/\text{m}^3$ concentrations of a large number of gaseous pollutants.

In most urban areas of the United States, the Environmental Protection Agency (EPA) requires of a number of air pollutants (eg, SO_2 , NO_2 and O_3), termed criteria pollutants, to be monitored with EPA designated methods. These methods are typically based on instrumental continuous monitoring principles and once designated by EPA are approved as Federal Reference Methods (FRM's) or Equivalent Methods. These FRM's are operated at fixed site locations. The EPA has an interest in comparing FRM ambient pollutant monitoring procedures at fixed sites with methods that determine the average concentration of the criteria pollutants over an open path. Comparisons between FRM's and a system such as a DOAS would assist in determining the influence of atmospheric pollutant inhomogeneities on FRM measurements and also assess the possibility of using long path procedures as FRM's.

In September and October 1989 a commercially available DOAS system was operated in the Research Triangle Park, NC. The system was programmed to measure SO_2 , NO_2 , O_3 , HCHO and HNO_2 . During this same period FRM measurements of SO_2 , O_3 and NO_2 were obtained at the same location as the DOAS spectrometer receiver for comparing fixed site and long path pollutant monitoring measurements. While all five of these pollutants were measured in this study, this report will focus on the DOAS and FRM measurements of SO_2 , O_3 and NO_2 .

Experimental

Federal Reference Methods. In this study sulfur dioxide measurements were made using a TECO Model 43 pulsed fluorescent SO_2 system (EPA equivalent analyzer EQSA 0276-009). The NO_2 measurements were made with a Combustion Engineering $\text{NO}-\text{NO}_2-\text{NO}_x$ Model 8101-B, operating in the 0-0.5 ppm range (EPA reference analyzer RFNA 0479-038). The ozone was measured using a TECO Model 49 UV photometric O_3 Analyzer operating in the 0-0.5 ppm range (EPA equivalent analyzer EQOA 0880-047). The FRM instruments were all calibrated at the beginning and the end of the study with standard calibration methods using dynamically generated gas mixtures. The ozone analyzer was calibrated with a TECO UV photometric O_3 calibrator model 49PS which was previously certified NBS traceable. Data from these reference methods were collected by a Campbell Model 21X data logger and hourly averages stored. Periodically data was retrieved from the data logger with a PC.

The reference analyzers were operating from the 2nd floor of the EPA Annex in the RTP, NC as shown in Figure 1. Ambient air samples were drawn into the monitors through a 4 meter by 4 mm ID Teflon tube inlet. The inlet was extended through the ceiling above the analyzers to an

outside sampling rain shield on the roof of the Annex adjacent to the DOAS receiver.

Description of Differential Optical Absorption Spectrometer. The DOAS light transmitter was positioned on the roof of the US EPA Environmental Research Center (ERC). The DOAS light receiver (Figure 1) was positioned on the roof of the EPA Annex adjacent to the inlets of the EPA reference analyzers. The light path was approximately 20 m above ground and passed directly over a portion of Interstate 40. Visible and ultra violet light from a xenon lamp, collimated by a parabolic mirror, passed through the outside air over the 557 m path from the roof of the ERC to the roof of the Annex. On the roof of the Annex the light from the xenon lamp is recollimated in a receiver assembly and focused onto the entrance fitting coupled to a fiber optic cable. The fiber optic cable transmits the light to a spectrometer, composed of a mirror, grating, chopper and photomultiplier tube, located 4 meters below in an air conditioned room. The DOAS system used in this study was calibrated to measure SO_2 , NO_2 , O_3 , HCHO and HNO_2 . The calibration³ of the DOAS is based on the use of reference gases introduced into special DOAS spectrophotometric cells of precise dimensions. The reference intensities and spectra are stored in the computer to statistically compare with ambient measurements to obtain concentration data.³

DOAS Measurements were performed by integrating for 1 minute the wavelength (selected windows from 260 to 460 nm) for each of the five pollutants in sequence. The computer processed the spectral absorption signal and displayed the updated concentrations for each pollutant every five minutes. Twelve one-minute readings were used to calculate the hourly average concentrations reported by the DOAS.

Results

Figures 2 and 3 are time series and correlation plots of DOAS and FRM measurements for SO_2 and O_3 obtained in September and October 1989 in the Research Triangle Park, NC. (similar plots were obtained for NO_2). These data show that in most instances the FRM's and DOAS measurements are in good agreement. As shown in Figure 3, during some short periods the DOAS O_3 values were significantly lower than the FRM values. These variations between the DOAS and FRM's may be explained by atmospheric inhomogeneities produced by such factors as the diffusion of nitric oxide (NO) emissions from mobile source traffic on Interstate 40 into portions of the DOAS absorption path. The nitric oxide rapidly reacts with the O_3 thus reducing the O_3 concentration in the open path compared to the FRM O_3 measurements. Conversely the small variations in NO_2 measurements between the DOAS and FRM may also be explained by the higher concentrations of NO_2 over portions of the DOAS absorption path associated with the roadway emissions.

During the study the SO_2 concentrations fell below the detection limit of the TECO pulsed fluorescence monitor. Also, the DOAS instrument appears to record SO_2 concentrations 2-3 ppb above the TECO instrument. The uncertainty in the calibration of the TECO SO_2 monitor is thought to be the source of this variation. The standards used to calibrate the SO_2 instrument are no better than $\pm 2\%$ at the 100 ppb level.

During the study there were several periods when the DOAS signal dropped to zero. These periods were associated with heavy rain and high humidity. Addition of heating tape to the receiver optics eliminated the fogging of mirrors in the receiver, which was thought to be part of the

problem. However, during periods of very high humidity, rain and fog, the light from the xenon lamp was scattered enough to interfere with the DOAS absorption measurements. This occurred for a few hours during the one month study.

The pollutants measured by DOAS are species that originate from a variety of sources in the troposphere. Since the monitoring was performed on the roofs of EPA facilities rather than at ground level, the influence of single vehicles or other point sources on the DOAS and FRM measurements was assumed to be minimal. The data from this study suggest this assumption was reasonable.

Conclusions and Recommendations

DOAS long path measurements for SO_2 , NO_2 and O_3 in Research Triangle Park, NC were in excellent agreement with FRM instrumentation. The correlation coefficients between FRM and DOAS were very high ($r > 0.9$) and showed no clusters of data. Some variations between the FRM's and DOAS instruments maybe associated with atmospheric inhomogeneities. The major advantages of the DOAS instrumentation are its low detection limits, ($0.5 \mu\text{g}/\text{m}^3$ for the 557 m absorption path for SO_2 , NO_2 , and O_3), multiple pollutant monitoring capability, long term calibration stability and rapid response characteristics.

A disadvantage of the DOAS system is the loss of signal during periods of fog associated with humid conditions. This maybe minimized by reducing open paths to 200-300 m. The DOAS system would be an excellent tool for measuring area concentrations of air pollutants to determine the sources of pollutants that impact air quality.

The DOAS instrument is capable of monitoring a number of gas phase air pollutants over different paths simultaneously. This multi-open path DOAS configuration will be evaluated this summer as part EPA's VOC/ O_3 study in Atlanta.

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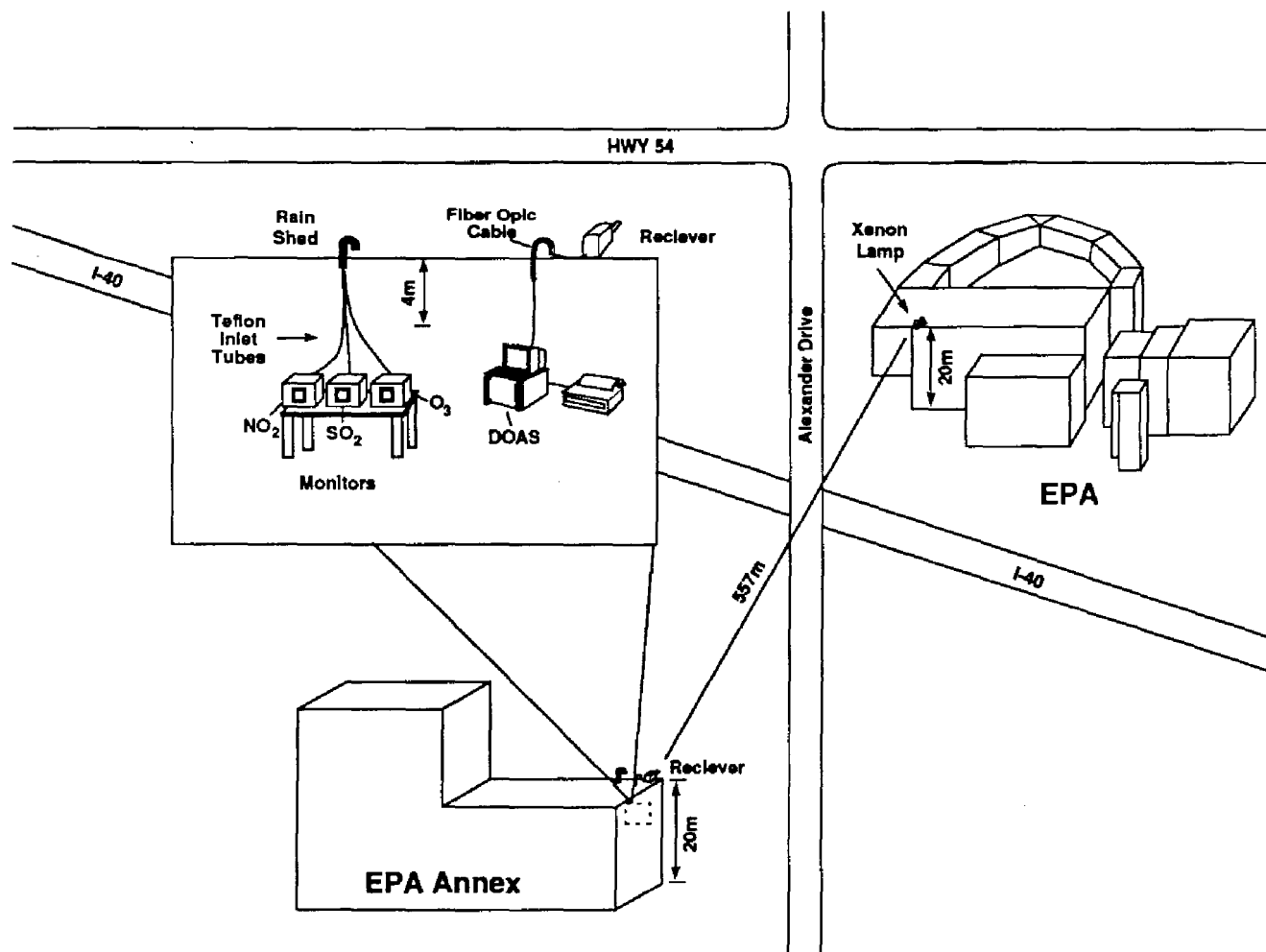


Figure 1. Location of the FRM's and the path over which the DOAS data in the Research Triangle Park, NC were obtained.

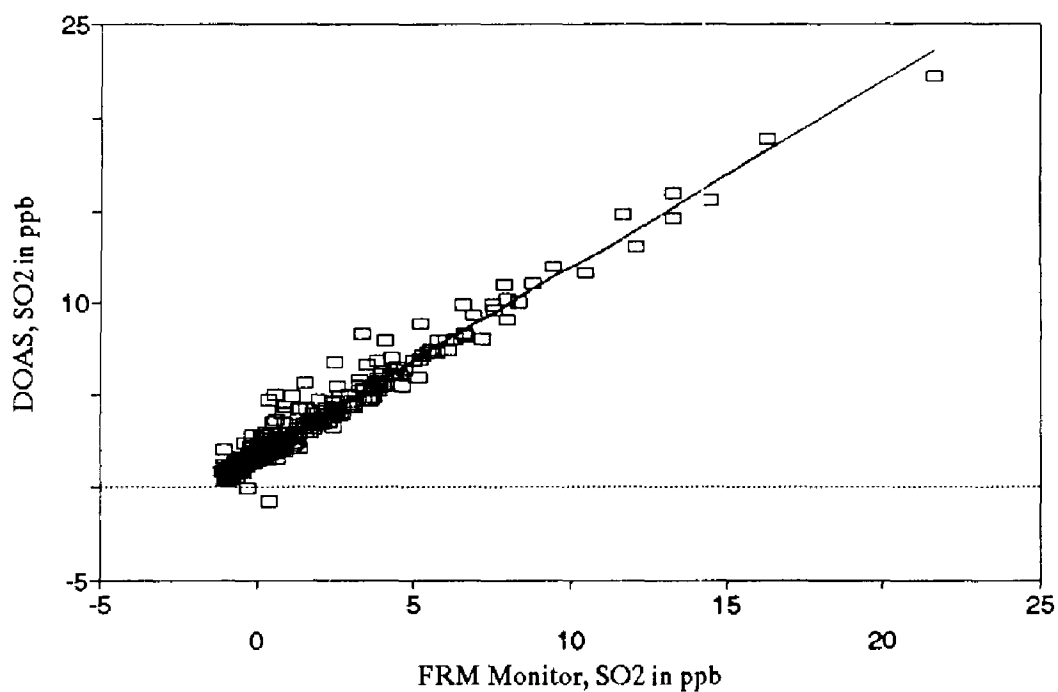
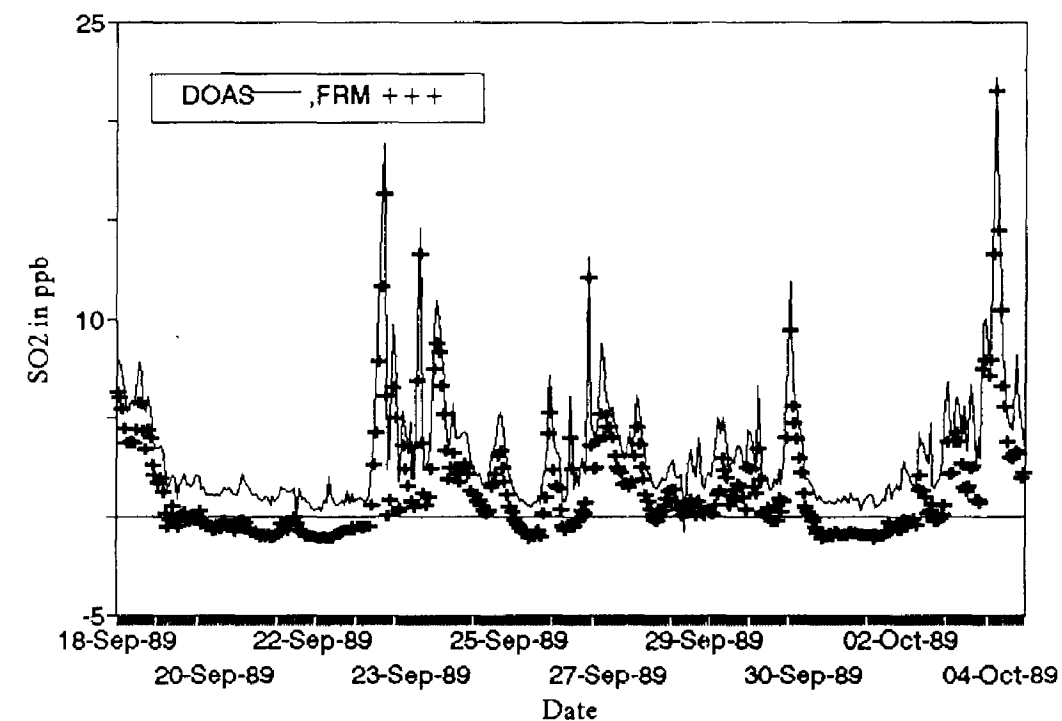


Figure 2. Time series (top) and correlation (bottom) plots of DOAS and FRM measurements for SO_2 obtained in Research Triangle Park, NC from September 18 to October 4, 1989. The square of the correlation coefficient is 0.96 and the regression equation is:

$$\text{DOAS}(\text{SO}_2) = 1.01 * \text{FRM}(\text{SO}_2) + 1.78$$

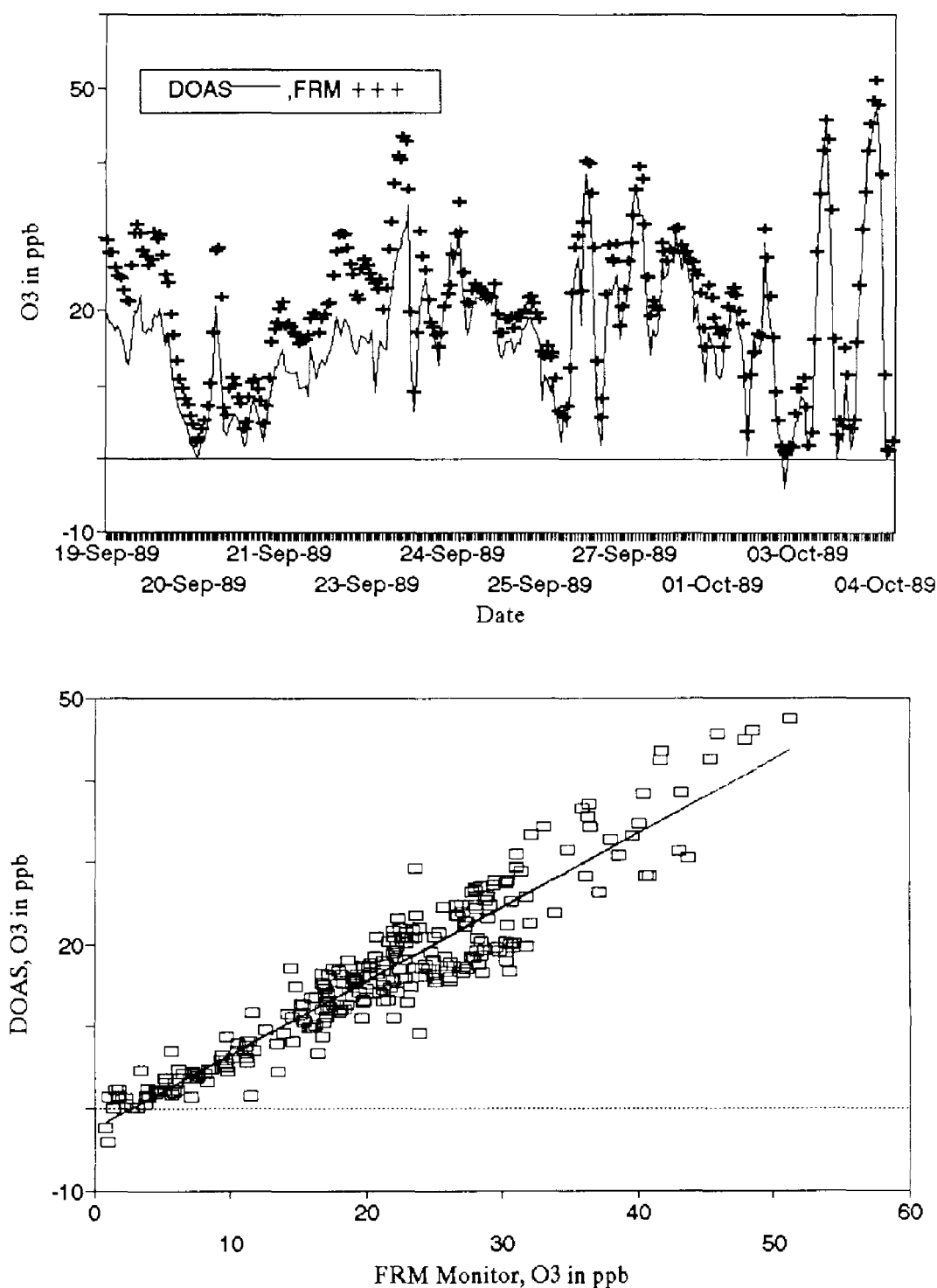


Figure 3. Time series (top) and correlation (bottom) plots of DOAS and FRM measurements for Ozone obtained in Research Triangle Park, NC from September 18 to October 4, 1989. The square of the correlation coefficient is 0.89 and the regression equation is:

$$\text{DOAS(Ozone)} = 0.90 * \text{FRM(Ozone)} - 2.46$$

Environmental control using long path measurements

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INTRODUCTION

Identifying, measuring and recording the types and quantities of molecules in a gaseous mixture has historically been very difficult. Gases comprise various types of molecules, and the problem has been to differentiate them in terms of qualitative and quantitative measurements. The technology known as differential optical absorption spectroscopy (DOAS) provides a solution to a large part of the problem. DOAS is a purely physical measurement method that is based on simple, well-known laws of physics.

An effective system for analysis of air pollution on the basis of DOAS technology was developed at the Department of Atomic Physics at the Lund Institute of Technology in Sweden by a group of research scientists that included Svante Wallin and Leif Unéus.

On the basis of their experience, Wallin and Unéus established the OPSIS company in 1985. Today, the company has more than 25 employees and is recruiting new personnel at an average rate of one per month.

The following presentation describes the measurement principles applied in OPSIS technology as well as a number of typical applications.

OP SIS measurement technology

The OPSIS system for analysis of pollutants in gaseous form measures the average value of pollutants in a beam of light between a transmitter and a receiver. An OPSIS system consist of the following units, as shown in Fig. 1:

- Transmitter
- Receiver
- Power pack
- Opto-analyzer
- Modem.

Measurements are based on optical absorption spectroscopy. Analysis of the parts of the spectra which are missing in the light received reveals the presence of various substances. Measuring the quantity of light that is missing enables the concentrations of these substances to be determined.

Quantitative determination is based on Lambert-Beer's law of absorption:

$$C = \frac{\text{Log } (I'o/I)}{(eL)}$$

where

C = concentration
I'o = light intensity before differential absorption
I = light intensity after absorption
e = average differential absorption
L = length of the absorption path.

The light from the transmitter is generated by a high-pressure xenon lamp in the form of a concentrated beam of light that includes wavelengths from short-wave UV to long-wave IR.

The receiver is trained on the transmitter, which captures the light and sends it over a fiber-optic cable to the opto-analyzer, the central unit in the system.

The opto-analyzer comprises a spectrometer, electronics for collection and processing measurement values, a hard disk, a computer for presentation and communication, and a modem.

As noted, light is sent from the receiver over a fiber-optic cable to the analyzer, in which it is broken up into spectra by a grating. This grating is mounted on a stepper motor that enables complete control of the wavelength interval. The spectrometer also contains a system of mirrors and a 50-mm photomultiplier. In front of the photomultiplier is a rotating disc with 20 axially oriented slits about 0.2 wide. The disc rotates at about 5 revolutions per second.

This arrangement enables about 40 nm of wavelength interval to be scanned in 10 ms over about 1000 channels, with a resolution of about 0.2 nm and an overlap of 80%.

The computer thus collects about 100 spectra per second of the wavelength in question. These spectra are converted to digital signals and stored in a multi-channel memory. The computer then compares these spectra with a pre-calibrated reference spectrum, wavelength by wavelength. Comparison can cover up to 1000 wavelengths, each of which contributes to the determination of concentration. A proprietary calculation program then computes the concentrations of the substances which the computer is programmed to analyze.

The program reports the margin of error for each measurement value and also reports on light transmission, i.e. it indicates how much of the light transmitted actually reached the receiver. These values can be used to check the function of the system.

The analyzer operates completely automatically. Measurement results are stored on the hard disk and can be presented on the VDU and/or a printer and can also be transmitted over the built-in modem to a host computer. The analyzer can also be remote-controlled through the modem.

Calibration

An OPSIS measurement instrument is calibrated by measuring a known quantity of a specific substance in the OPSIS laboratory, under precisely controlled conditions of pressure and temperature. The solvent content is determined on the basis of a table of steam-pressure data.

The absorption curve is stored in digital form, after which the instrument is ready for use. Recalibration is required only in exceptional cases.

An instrument which is often moved between measurement points should be zero-calibrated once a month using an OPSIS CA 075 calibration unit. Zero-calibration takes about 5 minutes per gas. In some cases, it may be necessary to check system performance using standard gases. This is a simple procedure and involves specially designed measurement cells of a precise length, normally 5-10 mm. The cell is connected with 2 fiber-optic cables between the analyzer and a transmitter fitted with the same type of lamp used in actual measurements. Gas is allowed to flow through the cell, and concentrations are recorded as in a normal measurement procedure. Three to five consecutive measurements are usually made for each gas, and possible deviations between measured and theoretical concentrations are adjusted with the change span and offset programs in the analyzer.

ESTIMATION OF ERROR MARGINS

Two types of error can arise during OPSIS measurements:

1. Absolute errors resulting from calibration faults, incorrect values for the measurement path, or incorrect values for temperature or pressure.
2. Relative errors, depending on the measurement instrument.

Absolute errors

Errors relating to calibration of gas normally deviate from the "correct" value by a maximum of $\pm 5\%$. The length of the measurement path can usually be determined to within $\pm 1\%$. Temperature and pressure can normally be measured with an accuracy of $\pm 1\%$.

Relative errors

The signal-to-noise ratio generates a maximum error of $\pm 0.5\%$.

It can be seen that the total error during normal measurements amounts in the worst case to about $\pm 8\%$. In most cases, measurement error is about $\pm 5\%$. Under extreme conditions, measurement errors of 10-15% have occurred.

MEASUREMENT

The flexibility of the OPSIS measurement system enables it to be used for a wide range of applications. The system is currently used for the following types of operations:

- A. Monitoring of pollutants in ambient air
- B. Monitoring of flue-gas emissions
- C. Process control
- D. Analysis of air pollution in the working environment.

I shall now briefly describe typical systems for these applications.

Monitoring of pollutants in ambient air

For surveillance of the air-pollution situation in a city, the transmitter and the receiver are normally positioned on rooftops, at distances of 100-2000 meters. The use of fiber-optic cable enables the analyzer to be installed in a sheltered place.

With a multiplexer connected, the analyzer can support up to 12 pairs of transmitters/receivers, which means that a very large area can be monitored within the city.

In Gothenburg, the second largest city in Sweden, four measurement stations have been positioned in areas with intensive pollution. Each measurement station includes 3-5 measurement paths of 200-2200 meters in length, for a total of 16 paths, which in effect covers the entire city. See Fig. 2.

All measurement data from these stations are transmitted together with meteorological data to a central computer, in which a specially developed program based on a dispersion model generates precise determinations of pollution levels. The results are used for traffic planning, among other things.

Almost 100 OPSIS systems have now been installed in Scandinavia and the rest of Europe.

Other applications for monitoring air pollution in ambient air include:

- Measurement of pollution at street level
- Monitoring of emissions from a factory
- Measurement of background emissions.

Fig. 3 shows a summary of the measurement parameters, measurement areas, detection limits and other factors which are relevant to the applications described.

Monitoring of flue-gas emissions

In terms of flue-gas monitoring, OPSIS has focused on systems for power plants, heating plants, co-generation plants and waste incineration facilities.

Precise, cost-effective control of emissions is a vital aspect of operations at modern power or heating plants.

OPSIS remote-controlled systems provide unique benefits for emission control. A single system can be used to measure SO₂, NO, NO₂, NH₃, Hg, H₂O and CO₂ at one or more measurement stations. A typical system configuration is shown in Fig. 4.

Emission control is also a very important activity in connection with incineration of household and/or industrial waste, particularly with reference to monitoring of HCl concentrations.

OPSIS systems have proved very attractive to operators of waste-incineration plants, as the technology provides fast, accurate information on concentrations of NO_x and Hg as well as other parameters.

Configuration and installation of OPSIS systems for these applications is similar to those for power and heating plants.

Process control

The great flexibility of OPSIS technology has led to installations for monitoring of a number of industrial processes throughout Europe, such as production of sulphuric acid. A single OPSIS system can be used to measure SO_2 concentrations, from strong gases with 10-15% SO_2 to residual gases where concentrations are measured in ppm.

NEW DEVELOPMENT

In terms of analysis, the OPSIS system has been expanded to cover sections of the infrared spectrum, up to about 1,800 nm. This involves fitting the analyzer with an extra grating and an IR-sensitive detector. A large number of hydrocarbons as well as a number of other substances can thus be detected and measured.

A combined receiver/transmitter system has also been designed, both fixed and computerised. These units are combined with retroreflectors that enable the wavelength of the light to be doubled, and thus provide a 100% increase in sensitivity. The retroreflector does not have to be installed on a fixed foundation, which gives greater flexibility for choice of measurement paths. This type of transmitter/receiver system can be mounted on a container or the roof of a car.

In conclusion, I would like to answer a question that is often asked, namely "How can we be sure that the values obtained are reliable?"

As previously mentioned, OPSIS technology is based on simple physical laws that have been well-known for many years. However, the technology is new in a commercial sense and our measurements have been repeatedly compared with conventional technology both in outdoor air and in process plants.

Figs. 5 and 6 show the results of several comparative tests.

SUMMARY

Feed-back from customers who have installed OPSIS equipment, from measurement assignments and from comparative tests has clearly shown that OPSIS measurement technology is highly reliable and that it has a very promising future. The main benefits of OPSIS technology include:

- No physical handling or preparation of samples
- High sensitivity and accuracy
- Large dynamic measurement area
- Measurement paths from 0.1 to 2000 meters
- Multipath measurements (12 per station)
- Simultaneous or sequential measurement of different substances
- On-site measurement and direct presentation of results
- Minimal calibration requirements
- Easy installation, ready-to-run
- Minimal maintenance requirements.

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Figure 1

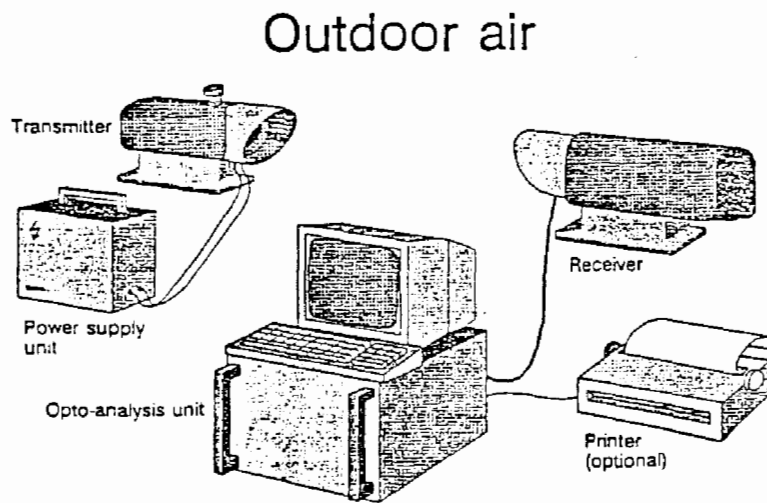
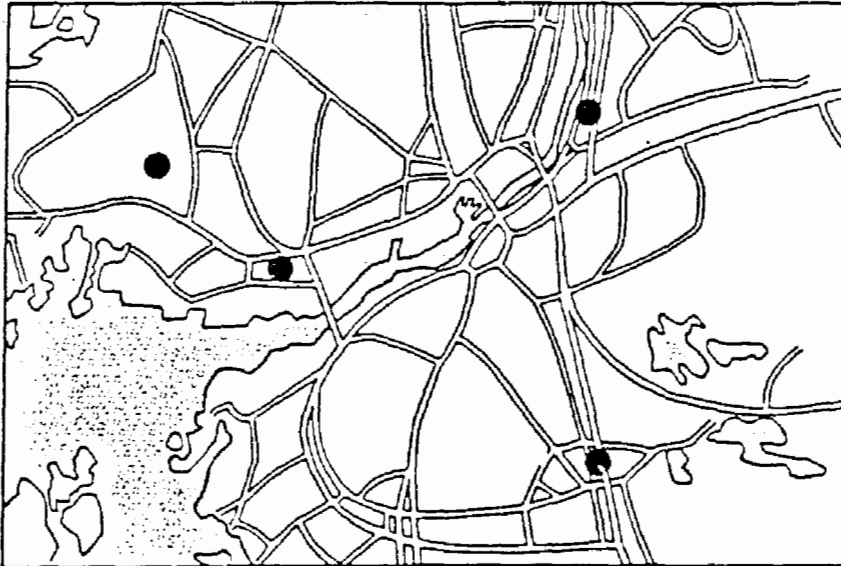


Figure 2



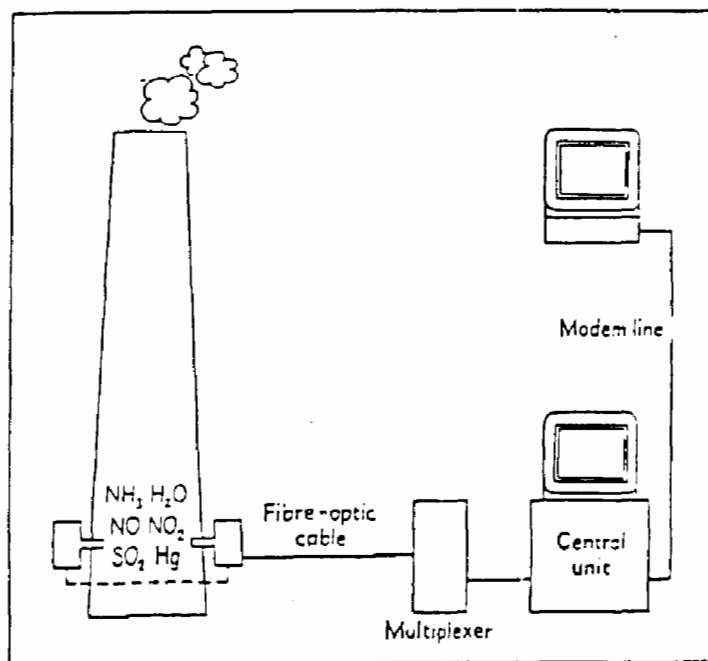
The four measurement stations are strategically located. All measurement data are displayed directly on a computer monitor at the office of the Gothenburg Municipal Association.

Figure 3

PERFORMANCE DATA

Parameter:	NO/NH ₃	NO ₂ /SO ₂	O ₂	NO _x	HNO ₂ /Formaldehyde	H ₂ O	Benzene/Toluene/Xylene
Measurement range:	0-2000 $\mu\text{g}/\text{m}^3$	0-2000 $\mu\text{g}/\text{m}^3$	0-2000 $\mu\text{g}/\text{m}^3$	0-500 $\mu\text{g}/\text{m}^3$	0-2000 $\mu\text{g}/\text{m}^3$	0-100 g/m^3	0-2000 $\mu\text{g}/\text{m}^3$
Minimum detectable quantities: (Monitoring path 500 m, measurement time 5 min)	2 $\mu\text{g}/\text{m}^3$	1 $\mu\text{g}/\text{m}^3$	3 $\mu\text{g}/\text{m}^3$	0.1 $\mu\text{g}/\text{m}^3$	2 $\mu\text{g}/\text{m}^3$	0.1 g/m^3	5 $\mu\text{g}/\text{m}^3$
Calibration Zero-point calibration	CA 075	CA 075	CA 075	CA 075	CA 075	CA 075	CA 075
Other calibration Zero-point stability (per month):	$\pm 4 \mu\text{g}/\text{m}^3$	$\pm 2 \mu\text{g}/\text{m}^3$	$\pm 6 \mu\text{g}/\text{m}^3$	$\pm 0.2 \mu\text{g}/\text{m}^3$	$\pm 4 \mu\text{g}/\text{m}^3$	$\pm 0.2 \text{g}/\text{m}^3$	$\pm 10 \mu\text{g}/\text{m}^3$
Linearity	$\pm 1\%$	$\pm 1\%$	$\pm 1\%$	$\pm 1\%$	$\pm 1\%$	$\pm 1\%$	$\pm 1\%$
Recommended length of monitoring path:	100-200 m	300-800 m	300-800 m	300-800 m	300-800 m	300-800 m	300-800 m
Maximum length of fiber-optic cable:	10 m	50 m	25 m	50 m	50 m	50 m	25 m
Hardware requirements:	AR 500						

Figure 4



Typical system layout for a power plant.

Figure 5

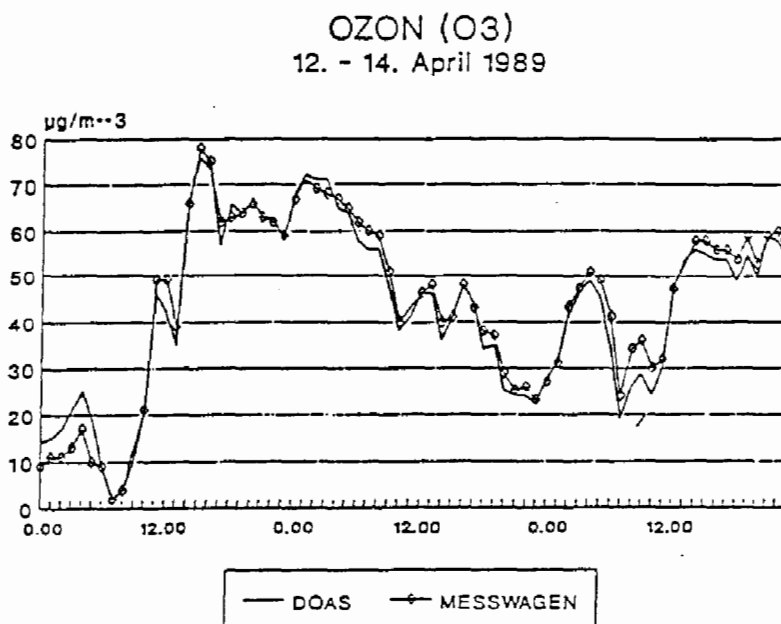
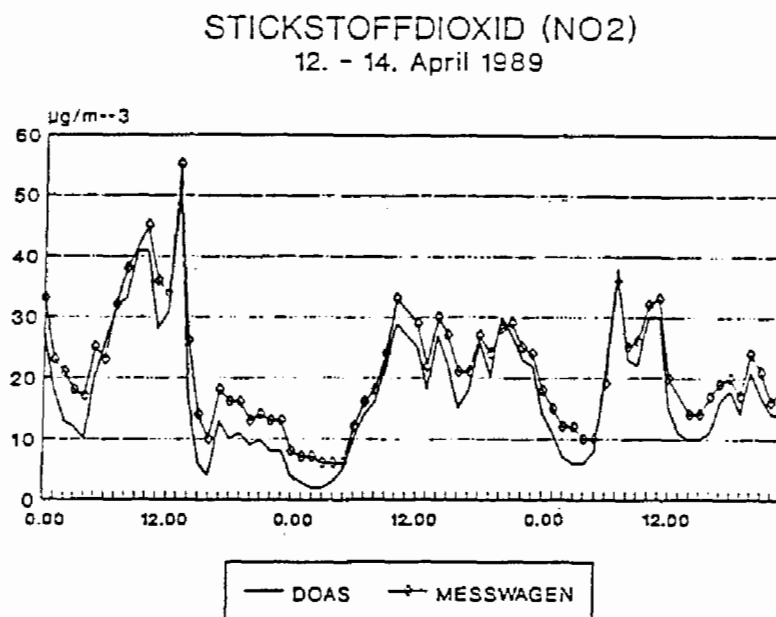


Figure 6



From: Kantonales Amt fuer Industrie, Gewerbe und Arbeit.
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**COMPARISON OF LONG PATH FT-IR DATA TO WHOLE AIR
CANISTER DATA FROM A CONTROLLED UPWIND POINT SOURCE**

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Two air monitoring techniques for atmospheric volatile organic compounds (VOCs): long path FT-IR and whole-air canister GC/FID have been tested simultaneously and the data compared. The long path FT-IR spectrometer system is being developed at Kansas State University to measure air toxics over varying distances. The whole-air canister GC/FID method has been used for several years at the University of Kansas for air toxics analysis and is an ideal system to test the performance of the FT-IR system.

The experiment, which took place at the University of Kansas, has the two techniques set-up co-planar with and perpendicular to a controlled upwind point source. The path length between the FT-IR spectrometer and source was varied between 50 and 232 meters. Five or six collection canisters were then placed directly along the IR path, evenly spaced, perpendicular to the wind-stack plume center line. The plume was generated from a 5 foot stack and allowed to drift unimpeded downwind to the co-monitoring systems. For these experiments the collected data were concurrently acquired over 12 and 27 minute time periods. During this time period meteorological data was also acquired for the calculation of concentration in ppb.

Many different parameters and compounds were tested during these co-monitoring experiments. The monitoring set-up, data analysis, various parameters of concern, and comparison of the two methods will be addressed.

Introduction

A field transportable Fourier transform infrared (FT-IR) spectrometer system for monitoring volatile organic compounds (VOCs) in the atmosphere is presently undergoing rigorous testing. A testing and evaluation plan was devised by Jody Hudson U.S. - EPA Region VII and edited by the Kansas State University (KSU) and University of Kansas (KU) groups.¹ The three phases of this plan are the controlled releases at KU, the uncontrolled releases at a well characterized site and the uncontrolled releases at a complex VOC site where little or no pre-test characterization data have been acquired. During phase one testing, many modifications were made to the FT-IR spectrometer system including instrumentation, data collection and data analysis. Some data have been accumulated in all of these phases, however the majority of work to date has been with controlled releases at KU.

Phase one will be the focus of this paper and presentation. This phase is broken into six parts which have been completed over the last year. These six parts were designed to find the practical limitations of the FT-IR system. The six areas are qualitative and quantitative measurements of single VOCs, qualitative and quantitative measurements of mixtures with similar and dissimilar VOCs, VOC detection limits, path length variations, meteorological parameters including humidity and wind velocity, and scattering by particulate matter.¹

The collection of data from phase one is now completed, with the exception of testing at different vertical heights. The data are being interpreted by both groups at present and the analysis will be completed in the near future. Comparisons between the KSU and KU data, taken in the spring and fall of 1989, exhibited differences in quantitative results². In the most recent measurements we attempted to address these discrepancies. The recent and past work will be discussed along with modifications to the experimental design and data collection, that may alleviate these discrepancies.

Experimental Methods

Equipment

The spectra are collected using a Bomem DA02 FT-IR spectrometer, equipped with a germanium on potassium bromide (Ge/KBr) beam splitter. This spectrometer is equipped with a f/4 input collimator and a f/1 fast output optic to the detector. A broad band MCT (Mercury Cadmium Telluride) detector, 5000-500 cm^{-1} , is operated at liquid nitrogen temperatures, approximately 77K. The instrument is purged with dry air from a portable air dryer. The collection optic is a 10 inch Cassegrainian telescope with an effective focal length of 150 cm, Figure 1. The primary source optic is a 20 inch f/4 paraboloid with the appropriate elliptical flat secondary optic and both are gold coated front surface mirrors. The Dobsonian mount for the mirrors forms a Newtonian collimating telescope. The infrared source, which is located at the focal point of the Newtonian collimating telescope, is a high temperature Nernst glower operated at 2073 K. The source is powered by a 1600 Watt portable generator. Distances between the source and instrument are measured accurately using electronic distance measuring equipment. Mobility is provided by a Journey mobile home designed to house and transport the necessary measurement instruments and crew.

Field Testing

The phase one testing at KU incorporated a single pass geometry with the IR source remotely placed from the spectrometer. The infrared source was placed at the focal point of the remote telescope to produce the collimated beam which was then passed to the spectrometer, Figure 2.

Various path length measurements at KU have been carried out from 50 to 232 meters. Initial observations at different industrial sites involved various open path lengths from 40 to 600 meters. In phase one, the KU group placed a VOC plume generator upwind and perpendicular to the IR path, Figure 3. Colocated along the IR path were 5 or 6 evacuated stainless steel canisters that were opened during the IR data collection to collect whole-air samples, see Figure 2. The stainless steel canisters are then analyzed using gas chromatography / flame ionization detection (GC/FID).

Procedure

Modifications to the FT-IR spectrometer have been recently made to alleviate discrepancies between the KSU and KU quantitative data. A silicon filter was placed just before the detector to mask the higher frequency region (when not needed) and only pass frequencies below 1600 cm^{-1} . This filter was added to cut down on the detector nonlinearity at high quantum fluxes. By masking out the high frequency region more low frequency energy may fall onto the detector and produce a better signal to noise ratio. The present scan parameters have been changed from our initial work and are compared in Table I. The spectrometers quantitative accuracy was tested by acquiring a spectrum of a 50 micron polystyrene film as a pre-test after every new setup. Polystyrene placed at the aperture before the actual data collection should afford a reproducible spectrum in frequency and intensity if the spectrometer is functioning correctly. This test is simple because polystyrene can be slid in and out of the IR beam between the input telescope and the aperture and polystyrene has a number of IR bands that can be readily measured.

The actual data acquisition has changed slightly as well and is as follows: measure instrumental emission, measure a background (upwind if possible or when VOCs are not being released) and then measure the sample spectrum. The background and sample spectrum are corrected for instrumental emission and are then ratioed to produce the absorbance spectrum. Originally, instrumental emission was omitted due to the long analysis time and what were believed to be small energy fluxes. Instrumental emission is now being acquired and taken into account to produce more correct absorbances.

Analysis

The resultant spectra are analyzed by interrogating the spectra by eye. The major absorbances from recognizable compounds are analyzed first, followed by major absorbances at unrecognized frequencies. The unknown frequencies are typed into a in-house frequency data base and are searched. These components are then stripped out of the absorbance spectrum using calibration spectra, if available, to obtain qualitative data, to obtain quantitative data and to reveal residuals. The residuals are then analyzed as previously mentioned.

Results

The qualitative results from earlier KU work were very encouraging to the authors; however, the quantitative results for this FT-IR method seem to be consistently lower than those for the canister method by 20 to 50 percent. These discrepancies were addressed and the system re-evaluated. The addition of the silicon filter for a decrease in saturation nonlinearities and the polystyrene as a standard test will afford us the ability to have the instrument performing the same in the field as in the laboratory calibrations. The very preliminary IR results from the recent KU project are seen in Table II. New calibration curves will be produced by using the new data acquisition method. 1,1,1-Trichloroethane was released at KU as a single component sample and the preliminary results from both

methods have been calculated. The whole-air canister data produced an average concentration over a 100 meter path length of 300 ppb. The FT-IR data analyzed this single component to be 175 ppb. This discrepancy could be a result of different vertical measuring zones in the atmosphere. The spectrometer when placed on the present tripod has a viewing height of approximately six feet. The stainless steel canisters were at a height of about 3 feet. Future testing at KU will address these height differences.

Qualitative and quantitative results were obtained for single component samples, for mixtures, for different IR path lengths, for varying meteorological conditions, and for particulate added plumes. None of these changes seemed to cause any degradation of the spectrometers performance. At longer IR path lengths however, the absorbances due to water and carbon dioxide can limit analysis in certain spectral regions. The mixtures tested at 100 meters had smoke added to the plume at the VOC generator as seen in Figure 3. The smoke was added to see what problems particulate matter would cause in the collection of the infrared data. No major problems were noted, however the IR beam was slightly attenuated by the smoke.

Conclusions

We believe that once the bias of the two data set techniques is within 5 to 10 percent with respectable precision the system will be site ready. Further research at the University of Kansas may be necessary to address height profiles of the VOC plume. Work is presently scheduled at a site in south central Kansas and other sites outside of Kansas. The Kansas site will include canister analysis to further help characterize the FT-IR systems capabilities.

Acknowledgements

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Disclaimer

Although the research described in this paper has been funded by the U.S. Environmental Protection Agency, it has not been subjected to Agency review and, therefore, does not necessarily reflect the views of the Agency, and no official endorsement should be inferred. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Table I

Initial and Present Spectrometer Scan Parameters Compared

Parameter	Initial	Present
Resolution:	0.1 cm ⁻¹	0.5 cm ⁻¹
Scan Speed:	1.5 cm/sec	1.5 cm/sec
Coadded Scans:	256 scans	512 scans
Apodization:	Boxcar	Hamming
Low pass filter:	50 KHz	10 KHz
Optical filter:	none	Si for <1600 cm ⁻¹
Data Acquisition Time:	27 min	12 min

Data may be taken at other parameters and still compared. This table is present to illustrate the variability of data acquisition.

Table II

Preliminary FT-IR Data from KU work in April 1990

Compound	Distance (m)	FT-IR Concentration (ppb)		
		Mixture 1	Mixture 2	Mixture 3
1,1,1-Trichloroethane	50	56	138	38
Methylene Chloride	50	136	31	106
Methylethyl Ketone	50	52	151	107
Toluene	50	35	85	233
t-Butanol	50	a	a	a
1,1,1-Trichloroethane	100 b	35	75	18
Methylene Chloride	100 b	80	31	63
Methylethyl Ketone	100 b	32	56	80
Toluene	100 b	18	116 c	146
t-Butanol	100 b	a	a	a
1,1,1-Trichloroethane	200	16	34	7
Methylene Chloride	200	42	13	29
Methylethyl Ketone	200	10	29	36
Toluene	200	20 c	30	42
t-Butanol	200	a	a	a

a Calibration curve on t-butanol has not been produced.

b Smoke was added to check the affect of airborne particulates.

c The major bands of toluene are strongly overlapped and measurement is difficult.



Figure 1 Coplanar alignment of the FT-IR spectrometer system with the evacuated stainless steel canisters. The IR source (not seen) is positioned just outside the frame on the left hand side.

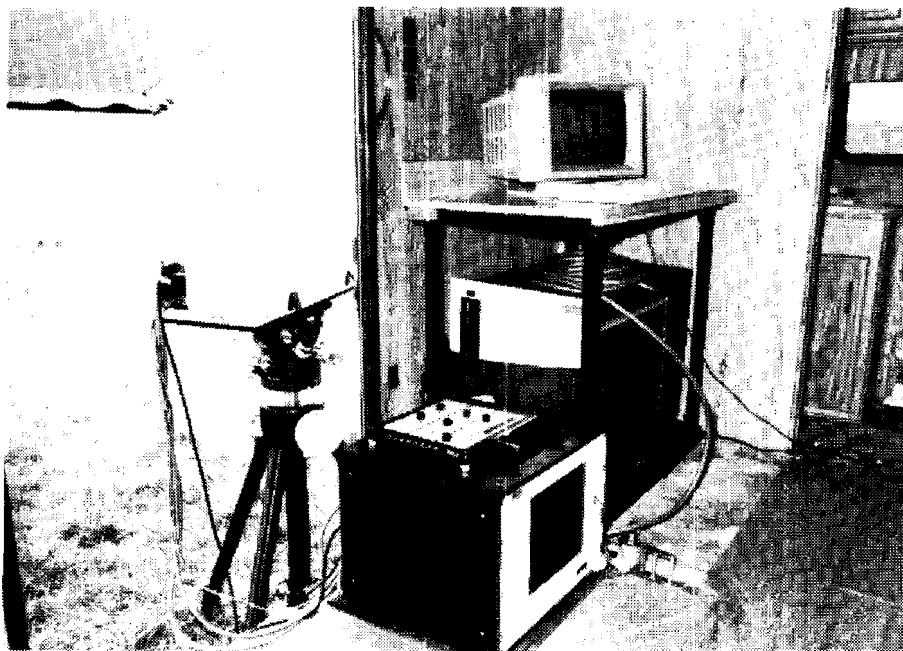


Figure 2 A picture of the inside back of the FT-IR mobile laboratory displaying the instrumental computer and spectrometer controlling electronics. The spectrometer can be seen just outside the cargo door upon the tripod and movement stage.

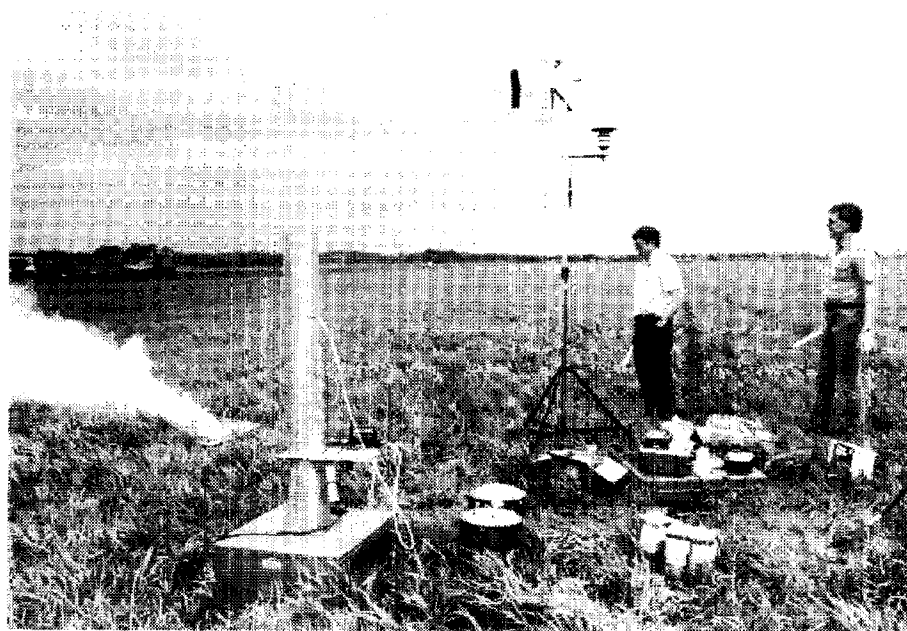


Figure 3 The University of Kansas plume generator, meterological station and smoke tray. The smoke was added to ascertain whether particulate matter will affect the FT-IR performance.

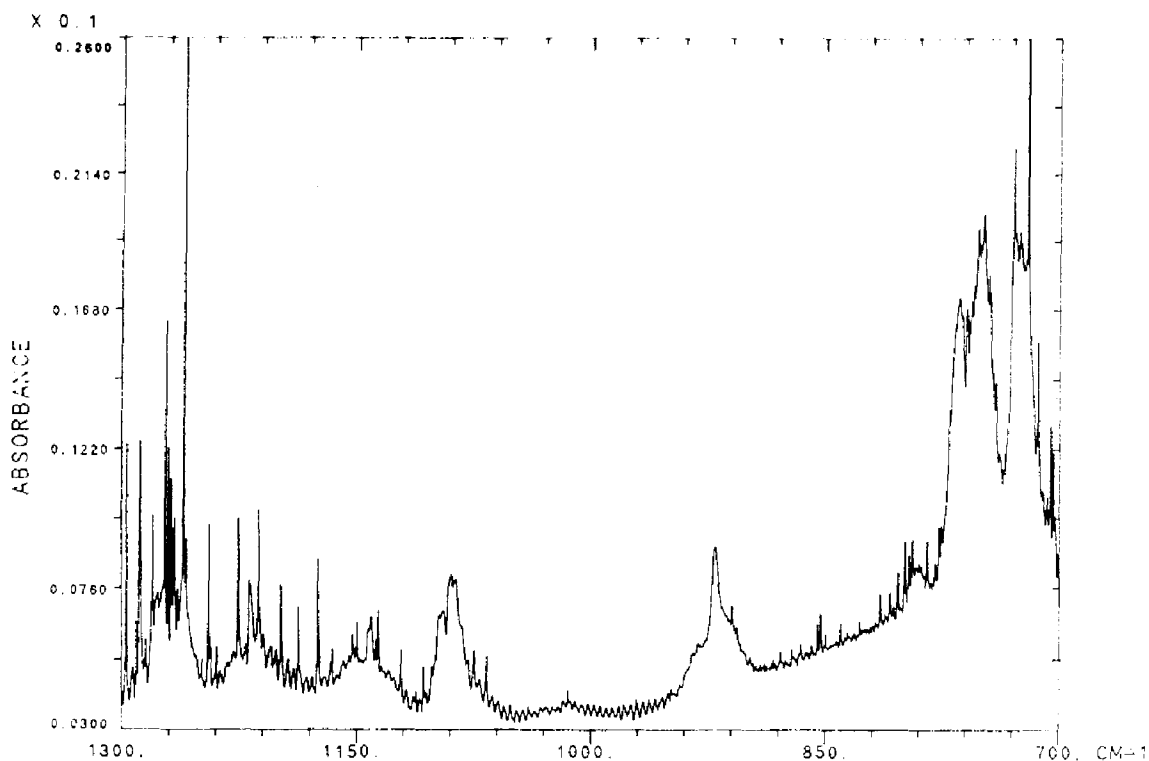


Figure 4 An atmospheric mid infrared absorbance spectrum of a five component VOC mixture generated at the University of Kansas. The spectrum is of mixture 1 at 100 meters. The compounds are 1,1,1-trichloroethane (726 cm^{-1} , 1090 cm^{-1}), toluene (729 cm^{-1}), methylene chloride (749 cm^{-1} , 1270 cm^{-1}), t-butanol (918 cm^{-1}), and methylethyl ketone (1174 cm^{-1}).

Analysis of Volatile Organic Compounds With An Ion Trap Mass Spectrometer

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The analysis of ambient air for trace levels of organic compounds in the field requires instrumentation which is sensitive and versatile but is not complicated in operation. This, of course, is not fulfilled by any one device or method of analysis. The ion trap mass spectrometer (ITMS) appears to at least address some of the desirable points mentioned. Therefore, an evaluation of the ITMS for detection limits using a direct inlet system was undertaken for 10 organic compounds in air. The instrument was able to detect the organic compounds in a high background of phosphoric acid. The detection limits for the compounds examined all appear to be in the mid ppb to low ppb regime. The detection limits for the aromatic compounds are conservative since these figures are based on 250 ppb standard. The overall detection limits are also conservative since the interface may still be improved. The ability to detect specific components in a complex mixture was evaluated using two air samples. The ITMS was able to determine a variety of components in these samples. The ITMS was able to confirm the identification of each of the components by mass spectrometry/mass spectrometry methods which yield a collision induced fragmentation spectrum characteristic of each component. Although this device is not commercially available for ambient air analysis these results suggest the instrument could fulfill many of the initial needs.

INTRODUCTION

The accurate measurement and determination of volatile organic compounds in the field requires a device which is sensitive, versatile, and easily maintained. Additionally, the device should be able to provide real time monitoring of the air being analyzed. The use of such a device would allow for an analysis of ambient air with a fast response time (minutes). One instrument which meets many of the attributes is the TAGA 6000 mobile MS/MS laboratory (1).

An instrument that is not commercially available as an ambient air analysis device but does have many of the above mentioned attributes is based upon ion trap technology (2-3). A number of research groups are currently evaluating similar instrumentation for volatile organic compound analysis in ambient air (4-7). The ion trap may be operated in a variety of modes including mass-selective storage (8-9). This mode of operation can be thought of as compound-selective storage, since it allows the device to be used to trap ions from a specific compound (i.e. ions having one m/z ratio) from a complex mixture of compounds. This connotes that the ion trap may be used to obtain very low detection limits in complex mixtures. Another advantage of this device is that it can analyze the selected compound (ion) further by use of fragmentation (MS/MS) techniques. The fragmentation techniques involves colliding the compound (ion) of interest with neutral molecules (collisionally induced dissociation [CID]) resulting in the formation of collision induced ion fragments which are characteristic of the compound and can be used to identify this compound in a mixture (10). The second MS/MS method technique that could be used is selective reactions, which are analogous to acid-base chemistry in the liquid phase, except the reactions occur in the gas phase inside the device (9).

R. G. Orth and coworkers presented a paper at the 1989 EPA/APCA symposium with preliminary data obtained using the ion trap mass spectrometer (ITMS) for ambient air analysis (11). This evaluation is an extension of the initial work utilizing different operational modes and interface. The evaluation included the determination of the detection limits of the ITMS for several compounds in calibrated mixtures sampled directly. A second evaluation of air samples was performed with the ITMS.

EXPERIMENTAL

Figure 1 shows a schematic cross section of the ITMS and the sample introduction system as utilized in this evaluation (3). The sample introduction system consisted of a fine metering valve and a heated transfer line. An uncoated megabore 0.83 μm (~ 3 meter) gas chromatographic column is used as a transfer line. The samples were analyzed using two ionization modes electron impact (EI) and chemical ionization (CI).

The samples were introduced through a fine metering valve, V1, to control the flow rate into the device. The static pressure of air in the device was generally 1×10^{-6} torr while the total pressure in the ITMS was in the 10^{-3} torr range. The difference in total pressure was due to the addition of helium (added co-axially to the sample inlet stream).

The samples analyzed for this analysis include NBS standards of a mixture containing benzene, toluene, chlorobenzene, and bromobenzene at concentrations of 10 ppm and 250 ppb per component in a bath gas of nitrogen. Certified standards from Scott Specialty Gas of a mixture containing acetonitrile, 1,3-butadiene, chloroform, carbon tetrachloride, and dichloromethane. The Scott standards were at concentrations of approximately 1 ppb, 10 ppb, 100 ppb, 1 ppm, and 10 ppm in a bath gas of nitrogen. Two air samples were collected in one liter Summa vessels and were analyzed.

RESULTS AND DISCUSSION

The air standard containing carbon tetrachloride was admitted directly into the ITMS via the sample introduction scheme in Figure 1. The majority of the sample is N_2 . Since the ion trap can be thought of as a box filled with ions from the sample, the predominate ions contained in the box would be those arising from N_2 . This makes it difficult to detect the ppm to ppb level constituents of interest, since the static pressure of the compounds of interest is on the order of 3×10^{-12} torr. To accomplish the detection at these trace levels, the device can remove the ions that arise from N_2 and any other ions which are not of interest (compound-selective storage).

Mass-selective storage provides a means for the minimization of interferences which originate at the trace level such as hydrocarbons. In the identification of carbon tetrachloride (CCl_4) for the standards, interferant ions present in the ITMS make the identification difficult. Figure 2a shows the result of combining the use of the ion trap in the mass-selective storage mode, i.e. selecting only m/z 117 to be stored in the trap and ejecting all other ions. The identification of m/z 117 as a characteristic ion from carbon tetrachloride can be accomplished by the use of MS/MS methods (10) (Figure 2b).

The detection limit was based on the signal (provided by the analyte) to the noise (present in the background) as established by continuously monitoring m/z 82 (the fragment ion of m/z 117) at 1 ppb, 10 ppb, 100 ppb and 10 ppm levels. The detection limit was determined to be ~500 ppb. This is a conservative detection limit since the interface for sampling was not maximized (i.e. the fine metering valve was unheated). The detection limits for both EI/MS and EI/MS/MS mode of operation are summarized in Table 1. The detection limits for the aromatic compounds are very conservative and are based upon data obtained from the 250 ppb and 10 ppm standards. The detection limits for the aliphatic compounds are based upon data obtained from standards ranging in concentration from 1 ppb to 10 ppm. The detection limits for all the aromatic compounds examined should be able to be improved to the low ppb to sub ppb regime. Three compounds in the mixture were unable to be quantified using the current experimental arrangement. Future work will include heating the metering valve and optimization of the data system which should allow for the quantifiable detection of all the components.

The second evaluation involved the analysis of two air samples collected using one liter Summa vessels. Sample one contained chloroform, since this was also used as a standard for

the earlier evaluation the concentration of chloroform was calculated to be ~100 ppb. Sample two was directly analyzed and the resulting electron ionization mass spectrum is very complex. The specificity of MS/MS is exemplified below using air sample two. This was done using collisional induced dissociation (CID) for each m/z ion which would represent a component in the summa vessel.

In the identification of benzene (C_6H_6) from air sample two, interferent compounds present make the mass spectrometric identification very difficult. The ions at m/z 77 can arise from a number of sources, but the ion at m/z 79 can arise from fewer sources such as protonated benzene or from hydrocarbons. Figure 3a shows the mass spectrum that results when the m/z ions 77-80 have been selectively retained (compound-selective storage). This is followed by kinetically exciting the m/z 79 ions and colliding them with He in the ion trap to yield the characteristic fragment ions of protonated benzene shown in Figure 3b. The fragments are typical for protonated benzene based upon knowledge of mass spectrometric fragmentation. Three components in sample two were identified by using EI/MS/MS analysis. This sample also contained ions associated with hydrocarbons which were not identified.

CONCLUSIONS

The ITMS from this evaluation has distinct promise as an analytical tool for the determination of trace organics in ambient air. The simple interface which samples air directly was shown to have detection limits in a complex background at the ppb to sub-ppb (carbon tetrachloride) levels for selected compounds. This limit is once again conservative and probably can be extended with improvements in the interface and data system utilized for this evaluation. The ITMS was able to identify and confirm the components of standard mixtures to the ppb region using EI/MS/MS. The ITMS was also able to identify components in two air samples by use of EI/MS/MS analysis. The small size of devices based upon ion trap technology (ITD and ITS40) indicate that the device may be miniaturized to a size that would be easily transportable (approximately the size of a gas chromatography system). Although near real time analysis was realized with this study, it should be possible with a properly designed interface and data system to obtain real time analysis.

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Table 1. EI/MS and EI/MS/MS Limits of Detection for Volatile Organic Compounds

<u>Compound (m/z)</u>	<u>EI/MS LOD's</u>	<u>EI/MS/MS LOD's</u>
Acetonitrile (42)	NQ ^a	NQ ^a
1,3 - Butadiene (54)	NQ ^a	NQ ^a
Benzene (77)	60 ppb	60 ppb
Benzene (78)	60 ppb	60 ppb
Dichloromethane (83)	5 ppb	5 ppb
Chloroform (84)	5 ppb	5 ppb
Toluene (91)	60 ppb	60 ppb
Chlorobenzene (112)	125 ppb	125 ppb
Carbon tetrachloride (117)	250 ppt	500 ppt
Bromobenzene (157)	NQ ^a	NQ ^a

^a NQ - Not quantifiable with current experimental arrangement

EXPERIMENTAL ARRANGEMENT

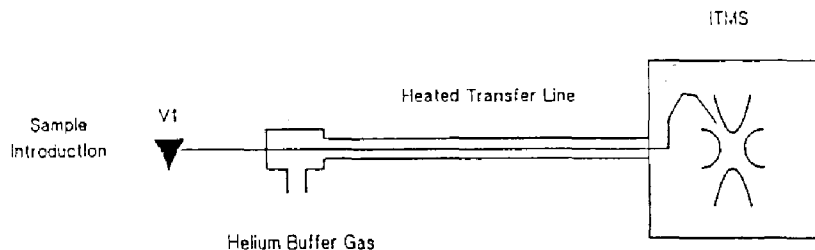


Figure 1.

Schematic of experimental arrangement for air sampling with the Ion Trap Mass Spectrometer.

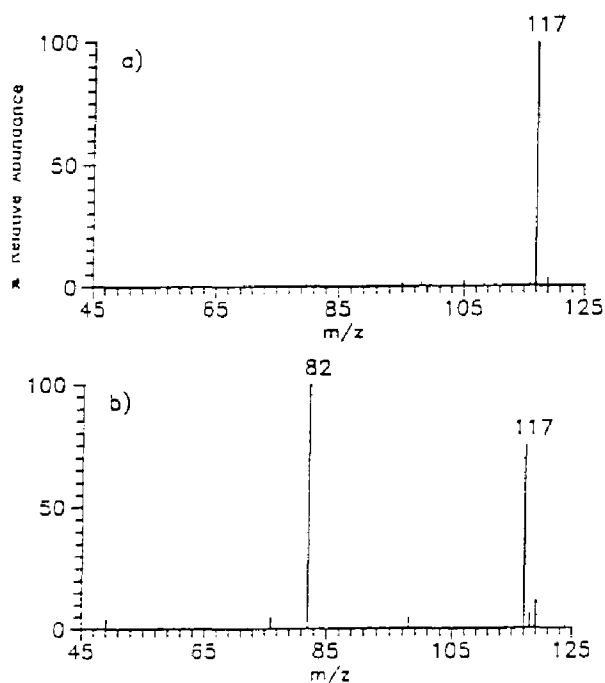


Figure 2.

a) Detection of carbon tetrachloride in the 10 ppb standard using selected mass storage.

b) The collisionally induced dissociation of m/z 117 which yields fragments characteristic of carbon tetrachloride.

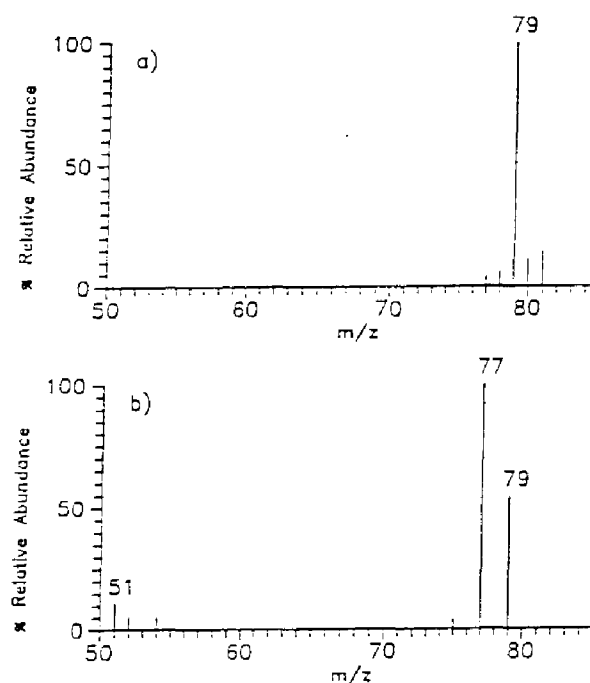


Figure 3.

a) The use of the ion trap to isolate m/z 77 to 80 where 79 is believed to be due to the protonated benzene molecule.

b) The collision induced dissociation of m/z 79 which yields fragments that represent protonated benzene.

Evaluation of a Non Cryogenic Automated Multitube Thermal Desorption System for the Analysis of Air Toxics

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Introduction

Improved methods¹ in air monitoring technology which employ multi-layer sorbent tubes, followed by Thermal Desorption/Gas Chromatography/Mass Spectrophotometry (GC/MS) have been shown to be a more efficient method for the collection and analysis of volatile organic compounds (VOC's), than existing preconcentration techniques. Despite its distinct advantages, the Thermal Desorption/GC/MS analysis of multi-layer sorbent tubes, suffers from the disadvantage that it is not amenable to total automation.

In an effort to automate the above mentioned "Improved Method," the Suffolk County Department of Health, working with Envirochem Inc. (Kembleville, PA) over a period of six months (12/88 - 5/89) evaluated and helped develop the Model #8916 Multiple Tube Desorber Unit (MTD).

This paper will discuss and evaluate an entire integrated air analysis system. The analytical system is composed of Envirochem's Model #8916 MTD, Envirochem's 810A Concentrator, Hewlett Packard Model 5890 GC and Model 5970 MSD.

Incorporation of the MTD in the abovementioned system, is shown to provide the following:

- (1) Automation Features:
 - (a) Increased productivity, unattended operation for the thermal desorption of 16 multi-layer sorbent tubes without the need for cryogenic focusing.
 - (b) Ability to back load sorbent tubes, therefore permitting extended use of GC/MS equipment.
- (2) Improved accuracy and recovery, particularly for more volatile compounds.
- (3) Improvement in overall Quality Assurance due to ability to run more standards and blanks.
- (4) Ease of Operation.

Principle of Operation

The MTD (see Figure 1.) employs an electronically controlled, air actuated 16 position multiport valve, to direct carrier gas flow through a preselected sorbent tube which is about to undergo a thermal

desorption cycle.

The start of the thermal desorption cycle is normally controlled by a remote start signal, received from the GC/MS; however an automode (w/o remote start), and a manual advance button can also be used to initiate a cycle, and/or advance positions.

A Typical MTD Cycle:

- (1) At the start of the thermal desorption cycle the MTD allows a 1 min purge of carrier gas, to free the sorbent tube and transfer lines of oxygen. This dry purge also acts as diluent and carrier for moisture in the analytical system.
- (2) Thermal desorption of sorbent tubes occurs with the aid of a sleeve heater at a flow of 60mL/min helium at a preselected temperature, for a preselected time.
- (3) Through the use of a heated transfer line the VOC's are then transferred to the large bore trap of the concentrator. (see Figure 1.)
- (4) After allowing additional time and flow for proper transfer of organics, the large bore trap is rapidly heated and the VOC's are transferred onto a micro bore trap.
- (5) Similarly, the micro bore trap is ballistically heated and a discrete slug of concentrated organics is transferred to the capillary direct interface of the GC/MS analytical system.
- (6) The MTD is instructed to start a new cycle via contact closures on the GC/MS, once the analytical run is complete and equilibration temperatures are reached.

Experimental

Materials

Envirochem ST-032 multi-layer sorbent tubes were utilized as the collection media. The air monitoring tubes were constructed of Pyrex glass (20cm long x 6mm OD and 4mm ID) and contained a glass frit, sequential layers of glass beads, Tenax, Amborsorb XE-340, and charcoal adsorbants.

Analytical standards were obtained from Aldrich Chemicals (Milwaukee, WI), Chem Services (West Chester, PA), and Scott Specialty Gases (Plumsteadville, PA).

A Supelco (Bellefonte, PA) model 2-3800 high capacity purifier, with an OM-1 indicating purifier was used to scrub ultra high purity helium of undesirable oxygen, moisture, CO, and CO₂, prior to entry into the analytical system.

Standard Preparation/Storage

Prior to use, air monitoring sorbent tubes are conditioned for 20 min at 310°C, while being purged at 60mL/min with ultra high purity helium. Upon completion of the heating cycle, with the aid of continued purge flow, the sorbent tubes are allowed to cool to room temperature, and are then placed in individually labeled glass/teflon screw capped storage containers.

After injection with an internal standard (4-bromofluorobenzene) the conditioned tubes are provided additional protection by storing dated batches of tubes in "Chain Of Custody" heat sealed 0.006 mil polyethylene bags.

After completion of sampling, the glass/teflon protected tubes are once again batch heat sealed in the polyethylene bags, and refrigerated @ 4°C to await analysis.

Standards were prepared using the EPA static dilution bottle method². Additional check standards were also employed, utilizing a Scott Specialty Gases certified blend of target compounds, contained in a single compressed gas cylinder.

All prepared gas standards were injected into conditioned sorbent tubes via septum in a pre-purged tee, which was housed in a 60°C oven. A purge flow of 60mL/min was continued for 5 min to assure complete transfer of VOC's onto the sorbent air collection tubes.

Analytical Parameters

M.T.D. - Temperature settings used were; valve compartment = 290°C, fitting compartment = 120°C, with all transfer lines set to 240°C. A complete 8 min cycle includes a 1 min prepurge (no heat) followed by 1 min heating cycle to 200°C, and finally a holding temperature of 200°C for the remaining 6 min.

Concentrator - After a 3 min secondary carrier flow time, the large bore trap was heated to 265°C in 22 seconds. A 3 min trap to trap transfer time was then used to translocate VOC's

to the micro bore trap. After the micro bore trap was heated to 275°C in 22 seconds, the total trap to column transfer and GC/MS run time was 52 min.

GC - A Restek (Port Matilda, PA) 60 meter, FITx Volatiles (crossbonded phenylmethyl polysiloxane), 0.25mm ID, custom made 1.5 μ film thickness, capillary column was used. The GC oven initial temperature was set to 0°C with a 2 min hold, then programmed at a rate of 2°C/min for 20 min, 4°C/min for 5 min, 7°C/min for 13 min, and 10°C/min for 7.9 min with a final hold time of 4.1 min (at the resultant 230°C temperature). The total run time was 52 min.

MS - Autotuned every morning with perfluorotributylamine. Ran at autotuned settings. During analysis the MS was operated in full scan mode from 19 amu to 260 amu.

Calibration is performed daily. System (MTD)/CONC/GC/MS) analysis of a sorbent tube calibration standard which contained a 34 compound toxic VOC mix, is illustrated in Figure 2. and listed in Table IV.

Results & Discussion

(Evaluation of Autosampler)

Thirty-five volatile organic compounds (34 toxic VOC's and 1 internal standard) were utilized to evaluate the MTD in conjunction with the entire concentrator coupled/GC/MS analytical system. Advantages and shortcomings are listed below:

- (1) Elimination of Cryofocusing - Moisture based chromatographic problems have been reported³ in systems which employ a cryogenic based trapping system. Semi-permeable membrane tubing (i.e., Nafion dryers) can be used on such systems to eliminate water, however such dryers also remove polar compounds. Therefore, one may be sacrificing the integrity of the original sample. Since the MTD does not employ the cryogenic principle, analytical difficulties associated with cryofocusing have been eliminated.
- (2) Increased Productivity - The labor intensive procedure of attended one-at-a-time desorption has been eliminated by allowing unattended sequential thermal desorption of 16 multi-layer sorbent tubes. Typically, before leaving for the evening, one "back loads" the MTD with additional air monitoring tubes; therefore, depending on analytical cycle time, 24 hour use of a GC/MS is now possible.

During unattended operation, the unit can be set into a dual remote start "safety mode", where, in the event of power failure occurrence, the maximum number of samples that can be lost is one (1). Once placed into the safety mode the MTD will not advance until the GC is "Ready" to accept samples.

- (3) Improved Precision and Accuracy - Individual "System Precision Checks" are listed for each of the target analytes in Table III. The mean imprecision for all 35 compounds was 4.9% R.S.D. (Relative Standard Deviation) which is lower than previously reported^{4,5} acceptable values obtained without the use of an MTD.

Since the EPA "Static Dilution Bottle" method used to prepare our standards, lists an imprecision of $\pm 10\%$, we find the analytical system to be extremely precise.

Improved accuracy, resulting from increased recovery of volatile organics (with a boiling point of less than 50°C) has been observed, when utilizing the MTD. Low or erratic recoveries often occur when employing a stand alone Model 810A Concentrator. When a sorbent tube is placed into the thermal desorption chamber of the Concentrator a purge flow goes over the tube to the vent position. Since the desorption chamber is at a temperature of 40-45°C this causes losses of highly volatile organics, especially if the sample is not fired immediately. This condition cannot occur when utilizing the MTD, because each sorbent tube is dead ended with no purge flow until the desorption cycle starts.

Results from our most recent EPA audit for Group V compounds are listed in Table V. With the exception of carbon tetrachloride quantitation accuracy at the 5ppb level was satisfactory (less than $\pm 30\%$ tolerance). Our poor results for carbon tetrachloride are currently under investigation.

- (4) Improved Quality Assurance - Ability to run more standards and blanks results in an overall improvement in quality assurance. For example, in a given 24 hour period, we have the ability to run a 5 point calibration curve, periodic check standards, field blanks, method blanks, and a post run standard, all appropriately sequenced into a normal sample run.

Additional System Checks

- (5) Linearity - The analytical system was found to be linear in the 0-50nL range for each of the target analytes. Results obtained for a 5 point calibration curve in a 32 compound mix, resulted in individual compound correlation coefficients ranging from 0.969 to 1.000, with an average of 0.993. Figure 2. shows a typical calibration curve.
- (6) Storage - Acceptable storage of VOC's ranged from less than 1 week for few of the extremely volatile compounds, to greater than 5 months for less volatile compounds. Please refer to Table I for compound specific storage information.
- (7) Break Through Studies - Results from a "100 Liter - Dry Purge" break through study indicated satisfactory recoveries for 31 of the 34 target compounds, inconclusive results were obtained for Freon 12, vinyl chloride, and bromomethane.

A similar break through study was conducted using a "100 Liters of 100% Humidified purge" flow. The humidified study indicated a 40% breakthrough for Freon 11, and a 50% breakthrough for methylene chloride. Inconclusive results were obtained for Freon 12, Freon 114, vinyl chloride and bromomethane. Recoveries for the remaining 28 compounds were satisfactory. Compound specific information is presented in Table II.

CONCLUSION

Use of the Multiple Tube Desorber (MTD) in the prescribed GC/MS system provides for automated analysis of air toxics without the need of cryofocusing. Improvements in productivity, precision, accuracy and overall quality assurance have been demonstrated.

Acknowledgements

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TABLE I. STORAGE STUDY

COMPOUND	STORAGE TIME IN DAYS		COMPOUND	STORAGE TIME IN DAYS	
	ACCEPTABLE	(b) INVALID		ACCEPTABLE	(b) INVALID
Freon 12	1	7	Tetrachloroethylene	150	-
Freon 114	4	-	1,2-Dibromoethane	150	-
Vinyl Chloride	1	7	Chlorobenzene	150	-
1,3-Butadiene	4	-	1,1,1,2-Tetrachloroethane	60	-
Bromomethane	1	7	Ethylbenzene	150	-
Freon 11	7	-	M-Xylene	150	-
Freon 113	7	-	O-Xylene	150	-
1,1-Dichloroethylene	7	-	1,1,2,2-Tetrachloroethane	60	-
Methylene Chloride	7	-	<u>Int.Std.</u> /Bromofluorobenzene	60	-
1,1-Dichloroethane	7	-	1,2,3-Trichloropropane	60	-
Chloroform	7	-	1,3,5-Trimethylbenzene	60	-
1,1,1-Trichloroethane	150	-	1,2,4-Trimethylbenzene	60	-
Carbon Tetrachloride	150	-	M-Dichlorobenzene	60	-
1,2-Dichloroethane	150	-	P-Dichlorobenzene	60	-
Benzene	150	-	P-Diethylbenzene	60	-
Trichloroethylene	60	-	O-Dichlorobenzene	60	-
1,2-Dichloropropane	150	-	Naphthalene	60	-
Toluene	150	-			

Note: (b) Invalid -less than 70% recovery.

Dashes indicate intervals not yet established.

TABLE II.

BREAK THROUGH STUDY

COMPOUND	100 Liter Dry Purge		100 Liter/100% Humidity Purge	
	(% Recovery)		(% Recovery)	
	Front Tube	Back-Up Tube	Front Tube	Back-Up Tube
Freon 12	---I	---I	---I	---I
Freon 114	90%	10%	---I	---I
Vinyl Chloride	---I	---I	---I	---I
1,3-Butadiene	100%	0%	100%	0%
Bromomethane	---I	---I	---I	---I
Freon 11	100%	0%	60%	40%
Freon 113	100%	0%	80%	20%
1,1-Dichloroethylene	100%	0%	83%	17%
Methylene Chloride	96%	4%	50%	50%
1,1-Dichloroethane	100%	0%	79%	21%
Chloroform	100%	0%	86%	14%
1,1,1-Trichloroethane	100%	0%	94%	6%
Carbon Tetrachloride	100%	0%	97%	3%
1,2-Dichloroethane	100%	0%	98%	2%
Benzene	100%	0%	100%	0%
Trichloroethylene	100%	0%	100%	0%
1,2-Dichloropropane	100%	0%	100%	0%
Toluene	100%	0%	97%	3%
Tetrachloroethylene	100%	0%	100%	0%
1,2-Dibromoethane	100%	0%	100%	0%
Chlorobenzene	100%	0%	100%	0%
1,1,1,2-Tetrachloroethane	100%	0%	100%	0%
Ethylbenzene	100%	0%	100%	0%
M-Xylene	95%	5%	95%	5%
O-Xylene	99%	1%	99%	1%
1,1,2,2-Tetrachloroethane	100%	0%	100%	0%
Int.Std./Bromofluorobenzene	100%	0%	100%	0%
1,2,3-Trichloropropane	100%	0%	100%	0%
1,3,5-Trimethylbenzene	100%	0%	100%	0%
1,2,4-Trimethylbenzene	100%	0%	99%	1%
M-Dichlorobenzene	100%	0%	100%	0%
P-Diethylbenzene	100%	0%	100%	0%
O-Dichlorobenzene	100%	0%	100%	0%
Naphthalene	99%	1%	99%	1%

Note: (I) Inconclusive results. Zero (0) or trace amounts only were found on the back-up tubes; however, less than expected amounts were found on the corresponding front end tube. Since sorbent tubes were prepared 7 days prior to analysis, reported storage problems may have caused or contributed to the low front tube recoveries. Further study is indicated.

TABLE III. SYSTEM PRECISION CHECKS

COMPOUND	AVG IN nL (n=3)	REL. STD. DEV. (%)	COMPOUND	AVG IN nL (n=3)	REL. STD. DEV. (%)
Freon 12	24.14	4.0	Tetrachloroethylene	5.40	3.5
Freon 114	24.28	3.4	1,2-Dibromoethane	6.62	2.4
Vinyl Chloride	22.72	9.7	Chlorobenzene	5.85	0.9
1,3-Butadiene	31.00	13.1	1,1,1,2-Tetrachloroethane	5.28	3.0
Bromomethane	22.05	12.9	Ethylbenzene	4.62	3.0
Freon 11	16.41	11.0	M-Xylene	4.73	2.1
Freon 113	4.65	3.7	O-Xylene	4.81	1.9
1,1-Dichloroethylene	6.54	12.8	1,1,2,2-Tetrachloroethane	5.98	3.0
Methylene Chloride	9.11	4.2	<u>Int.Std./</u> Bromofluorobenzene	5.26	1.9
1,1-Dichloroethane	6.36	4.2	1,2,3-Trichloropropane	5.60	1.6
Chloroform	6.97	2.6	1,3,5-Trimethylbenzene	4.33	1.6
1,1,1-Trichloroethane	5.48	4.9	1,2,4-Trimethylbenzene	4.24	1.7
Carbon Tetrachloride	5.57	5.0	M-Dichlorobenzene	4.77	8.0
1,2-Dichloroethane	7.21	3.9	P-Dichlorobenzene	6.36	3.9
Benzene	7.76	11.9	P-Diethylbenzene	3.67	5.2
Trichloroethylene	5.89	5.3	O-Dichlorobenzene	5.43	3.3
1,2-Dichloropropane	5.77	3.5	Naphthalene	20.15	6.0
Toluene	5.34	2.8			

Mean for 35 compounds _____ 4.9% R.S.D.

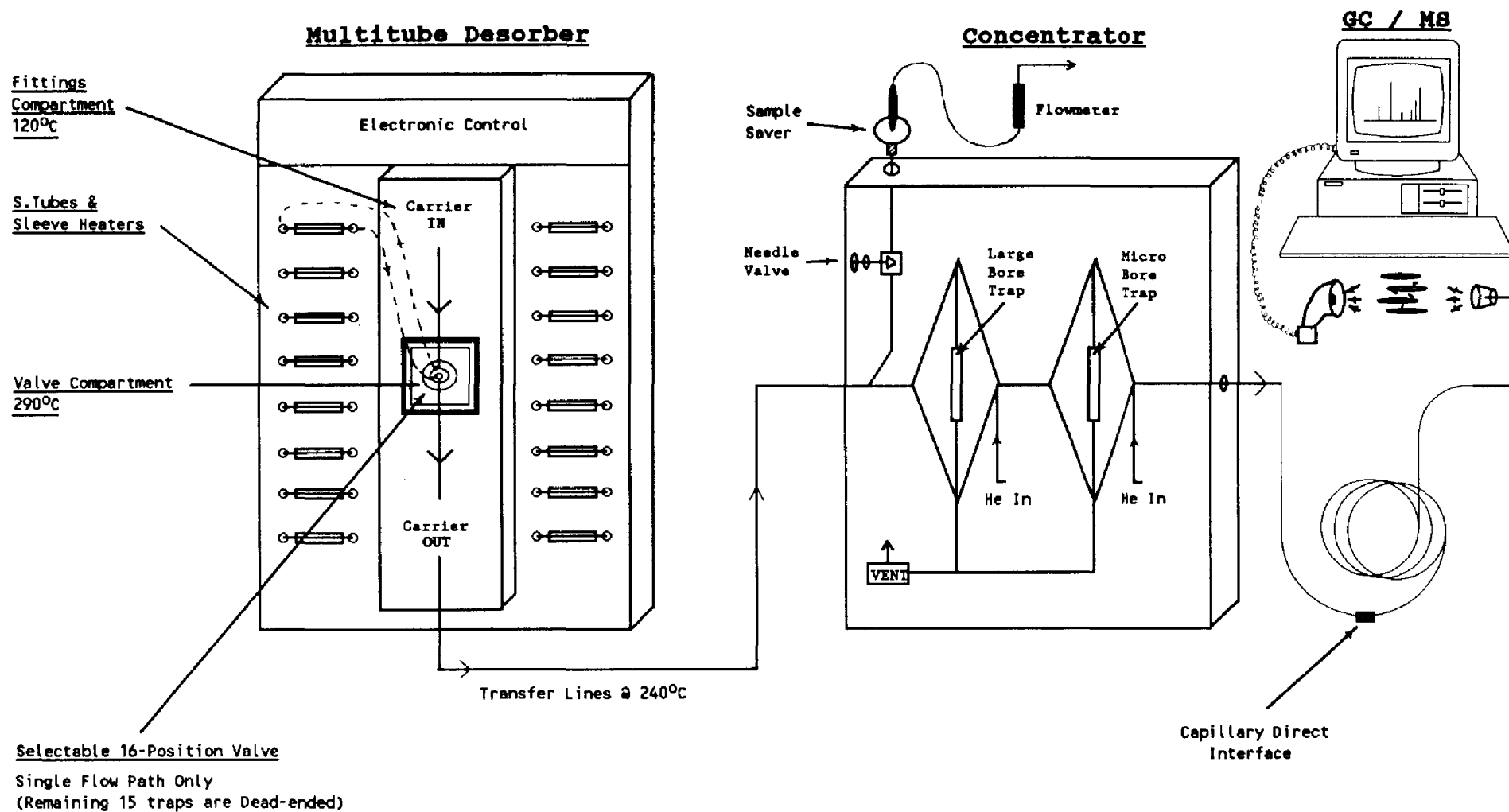
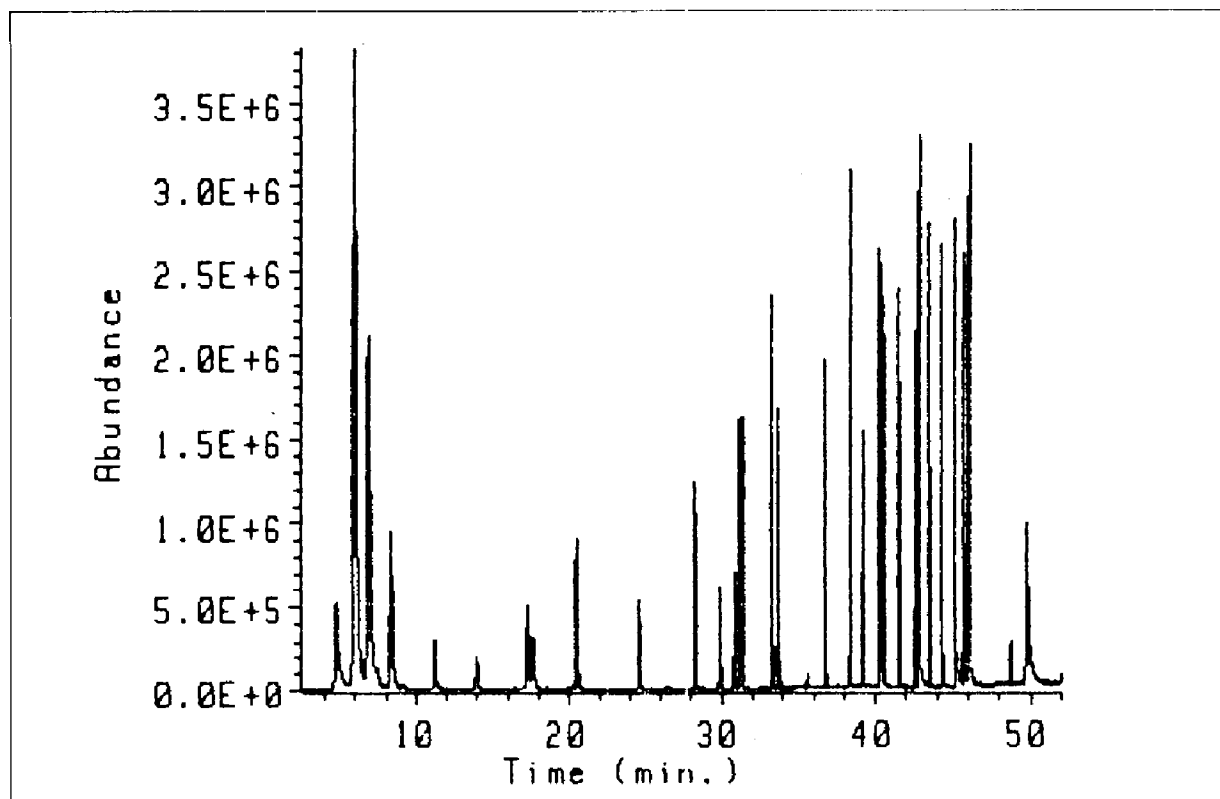


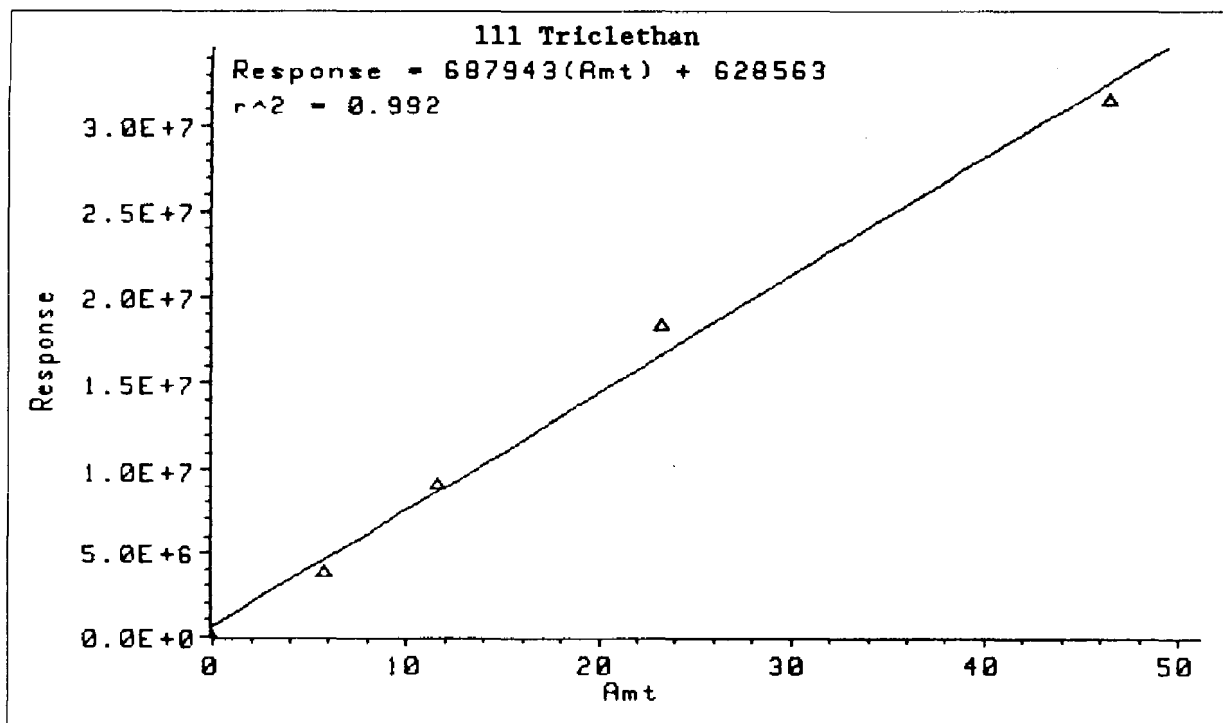
Figure 1. ANALYTICAL SYSTEM



**Figure 2. Chromatogram
(Calibration Std. S.Tube)**

Table IV. COMPOUND IDENTIFICATION

RETENTION TIME	COMPOUND	CONC. nL	RETENTION TIME	COMPOUND	CONC. nL
5.96	Freon 12	50.72	36.71	Toluene	11.08
6.90	Freon 114	50.72	38.35	Tetrachloroethylene	11.32
8.33	Vinyl Chloride	50.72	39.16	1,2-Dibromoethane	13.68
8.63	1,3-Butadiene	50.72	40.24	Chlorobenzene	11.82
11.18	Bromomethane	50.98	40.30	1,1,1,2-Tetrachloroethane	10.98
13.91	Freon 11	32.70	40.38	Ethylbenzene	9.60
17.25	Freon 113	9.70	40.57	M-Xylene	9.72
17.59	1,1-Dichloroethylene	15.38	41.54	O-Xylene	9.78
20.42	Methylene Chloride	19.08	42.56	1,1,2,2-Tetrachloroethane	11.44
24.57	1,1-Dichloroethane	13.44	42.81	Int. Std. / Bromofluorobenzene	10.80
28.23	Chloroform	14.42	42.86	1,2,3-Trichloropropane	11.44
29.84	1,1,1-Trichloroethane	11.62	43.49	1,3,5-Trimethylbenzene	8.76
30.80	Carbon Tetrachloride	11.70	44.30	1,2,4-Trimethylbenzene	8.54
31.12	1,2-Dichloroethane	15.06	45.10	M-Dichlorobenzene	10.08
31.30	Benzene	12.92	45.72	P-Diethylbenzene	7.40
33.24	Trichloroethylene	12.66	46.03	O-Dichlorobenzene	10.76
33.65	1,2-Dichloropropane	12.10	49.76	Naphthalene	11.22



**Figure 3. 5 Point Calibration Curve
(Linearity Check)**

**TABLE V. ACCURACY CHECK / EPA AUDIT
(Group V Cylinder - Unknown)**

	Reported Concentration P.P.B. (V)	
	Suffolk County Laboratory Results	R.T.I. (Reference) Laboratory Results
Vinyl Chloride	5.8	5.09+/-0.3
Chloroform	5.6	4.94+/-0.3
Carbon Tetrachloride	8.3	4.86+/-0.3
Methylene Chloride	5.0	4.28+/-0.5
1,2-Dichloroethane	5.8	5.26+/-0.4
Trichloroethylene	5.6	5.97+/-0.3
Benzene	4.8	4.50+/-0.3
Tetrachloroethylene	6.3	5.34+/-0.3
1,3-Butadiene	6.3	NA
Bromomethane	6.7	5.59+/-0.5
Freon 11	Storage Problem	5.00+/-0.6
1,1,1-Trichloroethane	5.7	5.20+/-0.3
1,2-Dichloropropane	5.7	5.33+/-0.3
1,2-Dibromoethane	6.2	5.10+/-0.5
Toluene	6.0	5.17+/-0.3
Chlorobenzene	6.5	5.33+/-0.4
Ethylbenzene	5.8	4.87+/-0.4
Ortho-Xylene	6.1	4.70+/-0.4

Stability/Instability of Gas Mixtures Containing
1,3-Butadiene in Treated Aluminum Gas Cylinders

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The Gas Metrology Research Group of the National Institute of Standards and Technology (NIST), formerly NBS, has been involved in research and development of gas standards of volatile toxic organic compounds for many years. Over thirty toxic organic compounds have been studied in gas mixtures contained in high pressure aluminum gas cylinders with specially treated interior surfaces. These mixtures, prepared using a microgravimetric technique developed at NIST, have been studied and tracked for many years to determine long term compositional stability. Almost all compounds studied to date have shown very good long term stability at the parts-per-billion (ppb, nanomole/mole) to parts-per-million (ppm, micromole/mole) range. One exception, 1,3-butadiene, is a compound that many scientists and policy makers are very interested in measuring in the environment. In this paper I discuss data obtained over several years for gas mixtures of 1,3-butadiene in nitrogen, at concentrations of 2 ppm, 100 ppb, and 10 ppb. The data demonstrate that mixtures of 1,3-butadiene at the 2 ppm level have remained stable for over three years. However, gas mixtures of 1,3-butadiene at the 10 ppb level have shown decreases in concentration of more than 70% over a two year period. Decreases in the concentration of 1,3-butadiene have been observed immediately after the preparation of the gas mixture in several cylinders. This work indicates that gas mixtures of 1,3-butadiene are not stable at the ppb levels and therefore are not reliable as accurate calibration standards. This suggests that fresh standards are needed to calibrate an instrument at the time of analysis and also that any "grab" samples containing this compound should be analyzed shortly after being taken.

Introduction

Concern has risen in recent years over the occupational health hazard from exposure to 1,3-butadiene, in particular its carcinogenic potential⁽¹⁾. EPA statistics show that there is an increased risk of cancer around several chemical facilities in the U.S., and that 1,3-butadiene is one of the compounds of concern⁽²⁾. A recent set of EPA data revealed that cancer risks to persons around some industrial facilities in the U.S. could be as high as one in ten. Political campaigners are using this data, as well as other, to press for stronger emission control provisions in the Clean Air Act⁽³⁾. Studies have been done that compare the permitted chronic human exposure to the chronic dose rate that induces tumors in a proportion of laboratory animals; the results showed 1,3-butadiene to be one of the most hazardous substances⁽⁴⁾. The current Threshold Limit Value (TLV) for 1,3-butadiene is 10 parts-per-million (ppm, micromole/mole) in the USA⁽⁵⁾ and also in the Netherlands⁽⁶⁾. Concerns over whether to decrease the TLV have been expressed, and as a result, Norway significantly reduced the permitted levels in the workplace atmosphere for a number of chemicals, including 1,3-butadiene, to 1 ppm⁽⁷⁾.

To properly monitor 1,3-butadiene levels in the workplace environment as well as the ambient atmosphere, accurate and stable calibration standards are needed. The Gas Metrology Research Group at the National Institute of Standards and Technology (NIST) has been studying, with support from the EPA, the feasibility of producing gas standards of 1,3-butadiene and other compounds in treated aluminum gas cylinders. As a result of this research, NIST developed gas standards for EPA to use in its quality assurance programs for ambient air monitoring of volatile toxic organics. Two of the groups of standards for EPA, Groups 4 and 5, contain 1,3-butadiene as well as other organic compounds.

Gravimetric standards have been prepared containing 1,3-butadiene ranging in concentration from 2 ppm to 5 parts-per-billion (ppb, nanomole/mole). These standards have been analyzed over time, with the introduction of new standards into the set at useful time intervals to determine the stability of the 1,3-butadiene gas mixtures. The results of these stability studies, and the feasibility of producing accurate, reliable, and stable standards containing 1,3-butadiene, are discussed.

Experimental

The aluminum gas cylinders used for the mixtures were treated by Scott Specialty Gases of Plumsteadville, Pennsylvania, using a proprietary process called "Aculife" to deactivate the cylinder walls. Gas standards containing 1,3-butadiene (and other organic compounds not common to every standard) in nitrogen were prepared in the aluminum gas cylinders using a micro-gravimetric procedure developed at NIST^(8,9,10). Several standards were prepared at each of three concentration levels: nominally 2000, 100, and 10 ppb.

The standards were intercompared using a gas chromatograph (GC) equipped with a flame-ionization detector (FID). Several different packed and capillary chromatographic columns were used depending on the other compounds present in the standards. A stainless steel gas sampling valve with a carbon filled teflon rotor was used to collect and inject the gas sample onto the column. The gas sample valve was equipped with a 1.0 mL stainless steel sample loop for analysis of the 2 ppm set of standards. A 10 mL loop was used for the 100 ppb standards. For analysis of the 10 ppb standards, an automatic cryogenic preconcentration system was used. The sample flow of 50 mL/min into the trap was controlled by a mass flow controller. The sample was typically collected in the trap for 5 minutes. The sample trap was then electrically heated and the sample was injected onto the GC column.

Since there is no absolute method to determine concentrations of organics at these levels, three methods were used to track the 1,3-butadiene concentration. Method 1 involved the correlation of the set of standards, at each level, using linear regression (a plot of gravimetric concentration versus GC area response). A concentration for each standard was then calculated from the linear regression fit. If the calculated concentration agreed with the gravimetric value, or the calculated value from previous analyses, then the compound was considered to be stable. Method 2 involved the preparation of new standards at selected time intervals and intercomparison of the old to the new standards. A ratio was calculated using the GC area response of the old to the new standard and a concentration was then determined based on the gravimetric value of the new standard. If the concentration determined for the old standard agreed with previous values, then the compound was considered to be stable. Any continuous decrease in the concentration outside of the uncertainty limits of the gravimetric concentration of the compound would signify instability. Method 3 involved the presence of an internal stable gas, such as benzene, along with the 1,3-butadiene in the standard. The GC area response for 1,3-butadiene was ratioed to the area response for the known stable compound. The standard was analyzed periodically by GC-FID and a ratio was determined. If the ratio changed in one direction continuously, then the suspected compound was not stable in the gas mixture.

Results and Discussion

Table 1 shows the results for a set of five standards containing 1,3-butadiene at the 2 ppm level. The gravimetric concentration, followed by the uncertainty of that value calculated from the sources of error (weighing, purity of starting materials) in the preparation, is given for each standard. The first four standards were prepared within four months of each other. Method 1 was used to intercompare the standards in 9/86 and in 5/89. The calculated concentration was determined from the linear regression of the analytical data. The results of that plot show excellent agreement ($r^2=1.0000$) for the set of standards and thus showed no decrease in the concentration of 1,3-butadiene in the four standards. However, this did not ensure that decreases were

not taking place. It was possible, although unlikely, that all the standards were changing at the same rate. To determine whether this was occurring, a new 2 ppm standard was prepared. Method 1 was used to intercompare two of the original four standards (the other two were not available) and the new standard. The linear regression, although only using three points, showed excellent agreement ($r^2=0.9995$) between the new and old standards, as shown under the column heading 9/89 in Table I. The calculated concentrations for these two original standards were identical to their gravimetric values determined in 1986. This data confirmed that the 1,3-butadiene in the gas mixtures at a nominal concentration of 2 ppm was indeed stable, and had been so for a three year period.

Only a few measurements of 1,3-butadiene stability were done at the 100 ppb level. Table II lists those standards that have been prepared and tracked for stability. Only method 2 has been used to measure the concentration of the 1,3-butadiene at this level. Standard AAL-19246 was compared to a 2 ppm standard, AAL-15885, in 4/87. Subsequent measurements were made by intercomparing the older standards to a new one. The two oldest standards, AAL-19246 and AAL-19249, decreased rapidly in concentration over six months and one month, respectively. Those two standards plus AAL-20701 were analyzed against a new standard, x-138356, shortly after it was prepared in 1/90. A further decrease in concentration was observed in each of the three standards, with AAL-20701 having decreased by an absolute amount of 19 ppb in one year. This represented the largest absolute decrease in 1,3-butadiene observed for any of the standards studied. The uncertainty in the gravimetric concentrations listed in Table II are a factor of ten smaller than the amount of decrease observed. Therefore, the data for these standards show that 1,3-butadiene is not stable in gas mixtures at the 100 ppb level, and one might predict similar results at the 10 ppb level.

Much of the work involving 1,3-butadiene in gas standards has been at the 10 ppb level. Many standards have been prepared and studied for stability. The data for a few of these standards are summarized in Table 3. The first four listed are the first standards prepared containing 1,3-butadiene at the 10 ppb level. Method 1, using linear regression of a set of standards, was used on the data from the intercomparison of these four standards in 10/86 and 4/87. The results show that standard AAL-17535 had decreased in 1,3-butadiene concentration from its preparation in 8/86 to 10/86 when it was first measured. The analysis in 4/87 indicated further decrease in AAL-17535 and a border-line decrease in AAL-15940 (the uncertainty bar overlaps the two values). Two of the standards, AAL-13377 and IL-3437, appeared to be stable for six months. Since the first four standards in Table 3 were intercompared using linear regression in 10/86 and 4/87, if one were to assume that all four of the standards changed a little, then the calculated concentrations may not show the actual changes in concentration because they are compared on a relative basis. To determine if indeed the first four standards in Table III had changed, two new standards were prepared in 1/88 and intercompared to the first four standards

in 2/88. Method 2 was used, ratioing the GC area response for the first four standards to the new standards. The 1,3-butadiene concentration was then calculated for each of the first four standards from the gravimetric concentration of the new standards. The resulting concentrations determined from these ratios show that indeed the older standards were decreasing. These results also show that the rate of decrease of the 1,3-butadiene is different from cylinder to cylinder, and therefore a constant rate change cannot be determined and applied to all cylinders.

Another set of standards are listed in Table IV. These standards, containing 1,3-butadiene at 10 ppb plus other organic compounds different from those discussed in Table III, were prepared and monitored as a function of time. Since IL-3437, from the original set, appeared to be stable for six months (see Table III, 4/87 analysis), it was intercompared with the five new standards prepared during 5/87. A response factor (GC area response divided by gravimetric concentration) was calculated for each of the standards. The response factors for standards IL-3437, AAL-19256 and AAL-19248 agreed within 1.6% of each other. All the other standards had response factors much less than these three. Therefore, method 1 was used to calculate the concentrations of the other standards listed in Table IV. The results show that the 1,3-butadiene had decreased in AAL-19254, AAL-19255 and AAL-19253, only one month after their preparation. This decrease continued when some of the standards were analyzed in 6/87. Two new standards were prepared and intercompared to this set in 1/88, using method 2. All the old standards had markedly decreased in concentration over the six months between analyses. Further decreases were seen again when part of the set was analyzed against a new standard in 6/88.

The results from these studies indicate that it is very difficult to determine what the actual concentration of the 1,3-butadiene is in a gas standard or mixture, at any given time, without preparing new standards. Even then, it is difficult to ensure the actual concentration since the 1,3-butadiene concentration might change between the time the standard is prepared and the time that it is first analyzed. To emphasize this point, and to follow the decrease of 1,3-butadiene in a gas mixture from the very beginning, a standard was prepared and regularly analyzed. This standard also contained benzene and toluene as internal standards, as well as some other compounds. Method 3 was used to follow the 1,3-butadiene concentration with time. The GC area response for a known stable compound, toluene, was ratioed to that of benzene, another known stable compound, to make sure the toluene was behaving as expected. The concentrations of 1,3-butadiene, toluene, and benzene were all nominal 10 ppb. At the same time, the GC area response for 1,3-butadiene was ratioed to that of benzene. Table V shows data for the ratio of the 1,3-butadiene GC area response to that of benzene and for toluene to benzene. The ratios for toluene to benzene did not change throughout the study which covered a period of over two years. However, the ratios of 1,3-butadiene to benzene show that there was a steady decrease of the 1,3-butadiene from the very beginning. The 1,3-butadiene in this standard decreased by 72% relative, representing the largest

relative decrease observed for any standard or mixture over such a time period. Other mixtures have been prepared and analyzed in the same manner with the outcome being the same.

The reason for the loss of 1,3-butadiene in the 100 and 10 ppb standards is not known, and it can only be speculated. During the study periods, no new peaks were found in the chromatograms from the analysis of these standards. Therefore, the reaction and formation of other compounds is probably not occurring, unless these possible new compounds are being adsorbed onto the cylinder walls. Another possibility for the decrease in concentration could be that the 1,3-butadiene itself is being adsorbed onto the cylinder walls. Polymerization of the 1,3-butadiene at active sites on the cylinder walls is also a possibility. The loss of 1,3-butadiene to heterogeneous polymerization would be minimal at these concentration levels since it depends on two molecules of 1,3-butadiene coming together at an active site on the cylinder wall. It would also be controlled by the number of active sites on the cylinder walls, which would vary from cylinder to cylinder. Since the 1,3-butadiene decreases in the 100 and 10 ppb mixtures, it may also be decreasing in those at the 2 ppm level. However, this same change in absolute concentration would not be as detectable in the 2 ppm standards because the analytical imprecision is on the same order as the observed decreases.

Conclusions

The research described here has shown that no degradation in concentration has been detected in gas mixtures containing 1,3-butadiene at the 2 ppm level, with 0.03 ppm precision. The gas mixtures were contained in treated aluminum gas cylinders, over a period of three years. Longer term stability at this concentration level is probable. Reliable and accurate standards can be prepared at this level and used to calibrate instruments for measurement and monitoring of 1,3-butadiene in the workplace environment. However, gas mixtures of 1,3-butadiene at the 100 and 10 ppb are not stable and are therefore unreliable even for short periods of time. The results in Table V show that 1,3-butadiene starts to decrease in concentration immediately after its preparation, and other data show that the amount of decrease varies from cylinder to cylinder. The data also show that it is very difficult to determine the concentration of 1,3-butadiene in a gas mixture unless a new standard is prepared and the analysis performed immediately. Even then, the concentration determined may not be accurate because the 1,3-butadiene concentration could decrease before the analysis can be performed. Anyone using stainless steel cannisters, or flasks made of other materials, should evaluate these containers for loss of 1,3-butadiene before using them for environmental or atmospheric sampling.

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Table I. Stability data for 2 ppm 1,3-butadiene in nitrogen standards in treated aluminum gas cylinders.

<u>Date Prepared</u>	<u>Sample Number</u>	<u>Gravimetric Concentration^a</u>	<u>Calculated Concentration^a</u>		
			<u>9/86</u>	<u>5/89</u>	<u>9/89</u>
5/86	AAL-5921	1.436±0.004	1.439±0.015	1.434±0.015	
8/86	AAL-15945	2.514±0.008	2.515±0.025	2.514±0.025	
8/86	AAL-15885	1.760±0.005	1.759±0.018	1.762±0.018	1.767±0.018
8/86	AAL-15941	1.650±0.005	1.652±0.016	1.646±0.016	1.645±0.016
9/89	x-138356	2.014±0.006			2.012±0.020

^a Concentrations are in ppm (micromole/mole) and the uncertainties are expressed as two standard deviations.

Table II. Stability data for 100 ppb 1,3-butadiene gas standards.

<u>Date Prepared</u>	<u>Sample Number</u>	<u>Gravimetric Concentration^a</u>	<u>Calculated Concentration^a</u>			
			<u>4/87^b</u>	<u>9/87^c</u>	<u>10/87</u>	<u>1/90^d</u>
4/87	AAL-19246	97.4±1.0	98.0	93.2	90.9	88.0
8/87	AAL-19249	138 ±1		138	131	129
12/88	AAL-20701	113 ±1				94
1/90	X-138366	106 ±1				

^aConcentrations are in ppb (nanomole/mole). The uncertainties for the calculated concentrations are ±1.0 ppb at two standard deviations.

^bConcentration determined by ratioing to a 2 ppm standard of 1,3-butadiene, AAL-15885 (see table 1).

^cConcentration determined by ratioing to AAL-19249.

^dConcentration determined by ratioing all the standards to X-138366.

Table III. Stability data for 10 ppb 1,3-butadiene gas standards.

<u>Date Prepared</u>	<u>Sample Number</u>	<u>Gravimetric Concentration^a</u>	<u>Calculated Concentration^a</u>		
			<u>10/86</u>	<u>4/87</u>	<u>2/88</u>
4/86	AAL-13377	18.9±0.4	19.0	19.0	13.8
8/86	AAL-15940	11.7±0.2	11.8	10.2	6.8
8/86	AAL-17535	22.1±0.4	18.4	14.8	9.3
9/86	IL-3437	15.4±0.3	15.0	15.4	10.8
1/88	CAL-11243	15.2±0.2			15.2
1/88	CAL-11233	3.9±0.1			4.0

^aConcentrations are in ppb (nanomole/mole). The uncertainties for the calculated concentrations are ±1.0 ppb at two standard deviations.

Table IV. Stability data for 10 ppb 1,3-butadiene gas standards.

<u>Date Prepared</u>	<u>Sample Number</u>	<u>Gravimetric Concentration^a</u>	<u>Calculated Concentration^a</u>			
			<u>5/87</u>	<u>6/87</u>	<u>1/88</u>	<u>6/88</u>
9/86	IL-3437	15.4±0.3	15.4			
4/87	AAL-19253	9.6±0.2	7.9	7.9	5.0	4.2
5/87	AAL-19254	13.2±0.2	11.9	11.4	8.1	
5/87	AAL-19255	12.3±0.2	11.0		8.8	
5/87	AAL-19256	7.4±0.2	7.3	7.1	4.6	3.6
5/87	AAL-19248	4.8±0.1	4.9	4.8	2.2	
1/88	CAL-11243	15.2±0.3			15.2	14.8
1/88	CAL-11233	3.9±0.5			3.7	3.6
6/88	AAL-20699	14.0±0.3				14.0

^aConcentrations are in ppb (nanomole/mole). The uncertainties for the calculated concentrations are ±1.0 ppb at two standard deviations.

Table V. Ratios of GC area response of 10 ppb 1,3-butadiene to benzene or toluene to benzene with time showing instability in gas standard AAL-19256.

<u>Date Analyzed</u>	<u>GC Area Response Ratios</u>	
	<u>1,3-Butadiene/Benzene</u>	<u>Toluene/Benzene</u>
5/18/87	0.667	1.23
5/19/87	0.661	1.22
5/20/87	0.659	1.22
5/26/87	0.597	1.19
5/27/87	0.585	1.20
6/03/87	0.563	1.19
6/19/87	0.525	1.23
1/19/88	0.366	1.20
6/07/88	0.328	1.21
7/01/88	0.292	1.22
10/05/88	0.250	1.23
12/07/88	0.243	1.21
1/10/89	0.237	1.22
8/01/89	0.185	1.20

TOXIC ORGANIC GAS STANDARDS IN HIGH PRESSURE CYLINDERS

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The accuracy of low ppb toxic organic gas mixtures in high pressure cylinders has been evaluated for a number of components in complex gas mixtures.

A review of the process taken to calculate the uncertainty will be described along with the experimental methods taken to minimize bias and improve precision. Results from such evaluation will be presented for several multi-component gas mixtures. Results from intercomparison of Scott standards with NIST standards will also be discussed.

1. INTRODUCTION

Several years ago, Scott Specialty Gases began manufacturing low concentration toxic organic gas mixtures, in response to the demand for standards to support analyses at EPA Superfund sites. Since that time, there has been a rapid increase in concern over environmental issues in general and significant improvement in analytical methods for low-level organics. The new Clean Air Act will mandate that more toxic organic measurements be made. Therefore, there is likely to be continuing demand for reliable standards covering an expanding list of compounds.

The subject of this talk is the Group V toxic organic mixtures. Scott has manufactured a series of cylinders containing 5 ppb of each of the following eighteen compounds in a nitrogen balance gas:

Bromomethane (Methyl Bromide)	Trichloroethylene
Dichloromethane (Methylene Chloride)	Tetrachloroethylene
Trichloromethane (Chloroform)	1,2-Dichloropropane
Tetrachloromethane (Carbon Tetrachloride)	1,3-Butadiene
Trichlorofluoromethane (Freon-11)	Benzene
Chloroethene (Vinyl Chloride)	Chlorobenzene
1,2-Dichloroethane	Toluene
1,2-Dibromoethane	1,2-Dimethylbenzene (o-Xylene)
1,1,1-Trichloroethane	Ethylbenzene

The Group V compounds are all important air toxics and are named on the EPA's target compound lists of extractable volatile organics.

The objectives of this paper will be to describe the steps in the manufacturing process for the Group V toxic organic mixtures and to discuss some of the quality characteristics of these standards, including concentration uncertainties and batch variability. Statistical methods for uncertainty calculations will be reviewed and the overall uncertainties of Scott mixtures will be contrasted with those for the NIST SRM 1804. Topics will be presented in the following order:

- Pre-Blend Preparations
- Blending
- Reference Standards
- Analyses
- Statistical Uncertainty
- Scott / NIST Intercomparison

2. EXPERIMENTAL

Pre-blend Preparations

The reagents which are used in these mixtures consist of organic materials and nitrogen balance gas. The organic reagents are purchased from commercial suppliers such as Aldrich and are assayed very thoroughly in our own laboratories by gas chromatography. The assay is important for two reasons. First, we need to detect any potential interferences (i.e., species that are present in one compound that will affect the concentration of another). Second, we need to know the overall purity of the material with some degree of certainty.

Nitrogen, used as the balance gas, is Scott's own Research Grade nitrogen (99.9999% purity), and is also analyzed prior to use. It is by far the largest component of the mixture. Therefore, interferences, even at the ppm level, are extremely important. A typical assay for Research Grade nitrogen is shown below:

Hydrocarbons (as Methane)	< 10 ppb
Halocarbons	< 2.0 ppb
Carbon Monoxide	< 5.0 ppm
Oxygen	< 5.0 ppm
Water	< 5.0 ppm
Other Impurities	< 1.0 ppm

Analyses show less than 10 ppb non-methane hydrocarbons. The hydrocarbons present are mostly ethane and ethylene, and therefore, do not interfere with any of the components in the mixture. The other impurities in the nitrogen do affect the overall certainty of the mixture, but do not interfere with any of the organic reagents in the mixture.

Cylinders are very carefully prepared prior to use. For mixtures of toxic organics, new aluminum cylinders of 30 liter capacity are purchased and equipped with a CGA 350 stainless steel packless valve. The cylinder is subjected to hydrostatic test to 3400 psi. Following the hydrostatic test, the cylinder is thoroughly dried and the valve/cylinder combination is then checked for gas leakage.

The cylinder is then subjected to our Aculife IV treatment. The Aculife IV treatment is a three-step process consisting of 1), a thorough deionized water wash, 2), extended heating and evacuation, and 3), treatment in the gas phase with a chemical which reacts with chemisorbed and structural water on the metal surface. The Aculife IV treatment is key to the stability of Group V organic mixtures.

The Aculife IV treatment has been able to produce stable mixtures of the compounds shown below:

Acetone	1,2-Dibromomethane	Freon 12
Acetonitrile	m-Dichlorobenzene	n-Hexane
Benzene	1,3-Dichloroethane	Methylene chloride
Benzyl chloride	1,2-Dichloropropane	Methylethyl ketone
Bromomethane	1,4-Dioxane	Perchloroethylene
1,3-Butadiene	Ethyl benzene	Toluene
Carbon tetrachloride	Freon 11	1,1,1-Trichloroethane
Chlorobenzene	Freon 113	Vinyl chloride
Chloroform	Freon 114	Vinylidene chloride
		o-Xylene

At Scott, new cylinder treatments are evaluated continually, but no treatment has yet been identified which can stabilize the organic compounds shown below:

Acrylonitrile	Formaldehyde
Aniline	Propylene oxide
Bromoform	Pyridine
Ethylamine	Styrene
Ethylene oxide	trans-1,4-Dichloro-2-butene

In general, compounds which are highly polar or which have strong hydrogen-bonding capability present stability problems.

Cylinder handling and gas transfer operations are accomplished using a specialized blending manifold. A great deal of care is taken with the components of the blending manifold. Only bellows or diaphragm valves are used. Stainless steel or nickel tubing is used throughout, and connections are either orbital welded or made using VCR-type fittings.

Blending

Blending, the process by which the components are combined at the proper concentration, consists of five steps:

1. A master liquid blending mixture of the fourteen liquid components is prepared in a glass container gravimetrically.
2. A master gas blending mixture is prepared by a three-step process:
 - A small quantity of the master liquid blending mixture is introduced gravimetrically to an evacuated cylinder by the Micrograv™ method. The Micrograv™ method is a variation of the glass capillary technique reported in the literature.
 - The four remaining gaseous components (Freon 11, vinyl chloride, bromomethane, and 1,3-butadiene) are introduced to the master gas blending cylinder gravimetrically.
 - Nitrogen balance gas is added gravimetrically. The final concentration of each of the eighteen components in the master gas blending mixture is 500 ppb.
3. The eventual product cylinder is connected to the blending manifold, evacuated and tared.
4. An appropriate quantity of the master gas blending mixture (eg, 50.0 g) is introduced to the product cylinder gravimetrically.
5. Finally, nitrogen balance gas is added to the product cylinder (eg, 5000 g) to achieve the final pressure and component concentrations.

Since all operations are performed gravimetrically, very low blending uncertainties can be achieved. Cylinders can be weighed to ± 0.1 g, yielding total uncertainties from 0.1 to 0.5%.

Reference Standards

Even though low blending uncertainties are readily achieved, adsorption/desorption phenomena can occur within the cylinder which change the blended concentrations of the organic components. Therefore, each cylinder must be analyzed and reference standards are required for the analysis.

Two sets of reference standards are required for the Group V toxic organic mixtures. One set covers the FID-responsive species (16 components) and the other covers the ECD-responsive species (Freon-11 and carbon tetrachloride). Standards at the appropriate concentration level are often not readily available for these mixtures, and therefore, it is necessary to generate our own reference standards.

The steps required to produce the FID reference standard are similar to those used to produce the original mixtures:

1. A second master liquid mixture of thirteen liquid components is prepared gravimetrically. This mixture is then diluted by a factor of 10,000 with a suitable solvent in order to give a weighable quantity of the liquid solution containing low concentrations of the organic components.
2. The FID standard itself is prepared in a glass flask by a two-step process:
 - A small quantity of the master liquid standard mixture is introduced gravimetrically into the glass flask, which had been pre-treated and evacuated to assure minimum container effect.
 - The three remaining gaseous components (vinyl chloride, bromomethane, and 1,3-butadiene) are introduced individually to the glass flask manometrically.

The glass flask mixture is used as a standard for gas chromatography analysis of the FID-responsive species. The glass flask is used to assign values to a secondary standard, a previously-prepared cylinder mixture (AAL 18488) of the eighteen components in nitrogen at 270 ppb. Although not essential to the certification process, this procedure provides a relatively large supply of the secondary standard with known values for future use.

Finally, a working FID reference standard at 10 ppb is prepared in a glass or stainless steel flask by diluting a small quantity of the 270 ppb standard by a factor of 27 using manometric techniques. The 10 ppb mixture is used as the standard for the analysis of the batch of Group V mixture cylinders.

The process for preparing the ECD reference standard is similar. A glass flask, similar to that used for the FID standard, is prepared and the two gaseous halocarbon materials introduced manometrically. No intermediate (secondary) standard is prepared.

Analyses

At this point, a batch of cylinders of the 5 ppb Group V mixtures, and two reference standards, have been prepared. Each cylinder in the batch can now be analyzed. One cylinder is selected at random from the batch to be the batch master. Since we have only limited quantities of the two reference standards available, the reference standards are used to assign values to the batch master, and then the batch master is used to standardize the remaining cylinders. As a QC measure, analyses are mixed over the course of the analysis process. The batch master is analyzed, then two batch cylinders, the batch master again, two batch cylinders, and so on. This procedure yields statistics for the batch master and a measure of long-term drift during the course of the analysis.

The conditions used for the gas chromatographic analyses are as follows:

FID-Responsive Species (All Except F-11 and CCl₄)

- HP 5890A FID
- 30 m x 0.53 mm DB-1 (Megabore)
- 9 cc/min Helium
- Temperature Program from 0°C to 165°C

ECD-Responsive Species (F-11 and CCl₄)

- Shimadzu Mini-2 ECD
- 6 ft x 1/8 in SP-1200 (packed)
- 25 cc/min P-5 (Argon/Methane)
- 80 °C Isothermal

Quality

The overall quality of these mixtures can be described by three key variables:

1. Individual component uncertainty
2. Individual component stability
3. Batch variability

Each of these key factors will be discussed separately.

Virtually every operation in the process, whether it be mechanical or analytical, carries with it some level of uncertainty. Uncertainties can arise from three main sources:

1. Repeatability (the precision of the measurement process)
2. Accuracy (the capability of the measurement device or technique)
3. Purity (assay of the mixture materials)

Uncertainties of all types are additive, ie, uncertainties accumulate as each succeeding operation is performed. The uncertainty of the final mixture can be determined mathematically by estimating the accumulated errors using the propagation of errors technique.

For any given operation, the incremental uncertainty can be calculated by taking the magnitude of the error associated with the operation, dividing it by the magnitude of the operation of itself, squaring that quantity, and then taking the square root of that result. A 95% confidence level can be achieved by multiplying the result by 200.

The overall uncertainty in the final mixture is the quadrature sum of the incremental uncertainties for all underlying operations, whether they are of the repeatability, accuracy, or purity type.

Our experience has shown the level of performance to expect from each step of the operation. The table below summarizes key process steps and typical relative uncertainties for the step:

<u>SOURCE</u>	<u>DOMINANT FACTOR</u>	<u>CONTRIBUTION</u>
Raw Materials	Purity	0.1%
Blending	Scale accuracy (mass dependent)	0.2 - 0.5%
Analysis	GC Precision (component dependent)	0.5 - 10%
Standards	GC Precision (component dependent)	0.5 - 10%

Well-characterized, pure raw materials contribute very little to the uncertainty of the mixture, 0.1% or less. For blending, usually performed gravimetrically, the relative uncertainty contribution is dependent on the capability of the balance being used and on the absolute mass of material being weighed. Using a balance capable of ± 0.1 g, even relatively small masses (eg, 50 g) can be measured with an incremental uncertainty of 0.2%. For multi-component mixtures, overall blending uncertainties range from 0.2 - 0.5%. For the analysis of the mixtures, the dominant performance factor is the repeatability of peak area in replicate GC analyses. For any given component, the incremental uncertainty contribution is dependent on the GC behavior of the component and can range from less than 1% to more than 10%. In general, compounds which elute late in the chromatogram or exhibit bad peak shape give poor analytical precision, and therefore contribute the highest amount of uncertainty in the final product. Total analytical uncertainties range from 2 - 10% for GC analysis, and this process step dominates the total uncertainty for the mixture.

There are a large number of individual operations that occur during the blending and analysis of an eighteen component toxic organic mixture. The total propagation of error calculation is extremely laborious to do, so much so that it is impractical to perform for every cylinder produced. Rather than perform the exhaustive propagation of errors calculation, Scott relies on a conservative estimate of 10% overall uncertainty for all components in a 5 ppb mixture. It is very unusual for a compound to exceed the 10% overall uncertainty criteria.

3. RESULTS

The first quality variable to be discussed is component uncertainty, i.e., the uncertainty for a given component within one cylinder. If the analytical value determined for the given component, and its associated uncertainty, includes the gravimetric blending value for that component, and its uncertainty, then that component is within specification. For example, a component is gravimetrically blended at 5 ppb, with a 0.5% relative uncertainty (or ± 0.025 ppb), and analytically determined to be 4.95 ppb, with a 5% relative uncertainty (or ± 0.25 ppb). The gravimetric value would be contained in the analytical value, and this result would meet Scott's criteria for component uncertainty.

The second major quality variable to be discussed is component stability. This variable is evaluated by performing replicate analyses over an extended period of time to observe concentration changes. A component is stable if the precision of replicate measurements made over the time period is within the 10% analytical tolerance. Stabilities for representative components studied over a nine month period are shown below.

<u>COMPONENT</u>	<u>2/20/87</u>	<u>11/9/87</u>	<u>% DELTA</u>
Chloroform	9.092	9.072	0.22
Benzene	8.873	8.408	5.20
Vinyl Chloride	9.644	9.905	2.70
Toluene	9.114	9.057	0.63
Bromomethane	9.815	9.374	4.50

The third and final major quality variable is batch variability, or the variability of a given component within a lot of identical cylinders. For a given component, this parameter is evaluated by calculating the ratio of the analytical value in the batch master to the analytical value for that same component in another cylinder from the batch. The calculation is repeated for each cylinder in the batch and statistics are performed on the set of ratios. A component values are identical within the batch if the precision of the analytical value ratios is within the 10% analytical tolerance. As can be seen in the table below, certain of the Group V toxic organics (bromomethane and 1,3-butadiene) exhibit unacceptable batch variation. NIST is unable to certify these components in the Group V mixtures for this reason.

Freon 11	1.6%
Benzene	2.2%
Chloroform	2.4%
o-Xylene	3.2%
1,3-Butadiene	13.2%
Bromomethane	15.6%

The table below shows a comparison of Scott Group V toxic organic standards to the NIST Standard Reference Material 1804. The first three columns show the Scott gravimetric value, the Scott analytical value, and the Scott total uncertainty (based on the 10% analytical tolerance criteria). The final two columns show the NIST analytical value and the calculated tolerance or uncertainty. The Scott analytical value, with the 10% tolerance, includes both the NIST analytical value and the Scott gravimetric value for virtually every component. Further, the NIST analytical value, with its published tolerance, includes the Scott analytical value for most components. It can be concluded that the Scott cylinders and the NIST cylinders are essentially identical, except for the large estimated uncertainty associated with Scott values.

<u>COMPOUND</u>	<u>SCOTT GRAV.</u>	<u>SCOTT ANAL.</u>	<u>SCOTT TOL.</u>	<u>NIST ANAL.</u>	<u>NIST TOL.</u>
Benzene	5.0	5.2	± 0.5	5.0	± 0.1
Bromomethane	5.0	5.2	± 0.5	5.4	---
1,3-Butadiene	5.0	5.4	± 0.5	4.6	---
Carbon Tetrachloride	5.0	4.6	± 0.5	5.0	± 0.1
Chlorobenzene	5.0	5.5	± 0.5	5.0	± 0.2
Chloroform	5.0	5.0	± 0.5	4.9	± 0.2
1,2-Dibromomethane	5.0	5.6	± 0.5	5.0	---
1,2-Dichloroethane	5.0	5.2	± 0.5	5.0	± 0.2
Dichloromethane	5.0	5.1	± 0.5	5.1	± 0.3

<u>COMPOUND</u>	<u>SCOTT GRAV.</u>	<u>SCOTT ANAL.</u>	<u>SCOTT TOL.</u>	<u>NIST ANAL.</u>	<u>NIST TOL.</u>
1,2-Dichloropropane	5.0	5.2	± 0.5	5.0	± 0.2
Ethylbenzene	5.0	5.7	± 0.5	4.7	± 0.2
Tetrachloroethylene	5.0	5.4	± 0.5	5.0	± 0.2
Toluene	5.0	5.2	± 0.5	4.9	± 0.2
1,1,1-Trichloroethane	5.0	5.3	± 0.5	5.0	± 0.1
Trichloroethylene	5.0	5.2	± 0.5	5.0	± 0.2
Trichlorofluoromethane	5.0	4.9	± 0.5	5.1	± 0.1
Vinyl Chloride	5.0	5.2	± 0.5	5.2	± 0.2
ortho-Xylene	5.0	6.0	± 0.5	5.1	± 0.2

4. CONCLUSION

Scott Specialty Gases, therefore, represents a commercial source for reliable standards for toxic organic work with near-NIST quality. Many other mixtures of similar quality are also available.

HUMIDIFIED CANISTER STABILITY OF SELECTED VOC'S

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ABSTRACT

In the environmental monitoring field the need for reliable standards for auditing and documenting data is well established. An important factor to take into consideration when such standards are prepared in canisters is the stability of the VOC's for the duration of time that they are to be used. Stability studies involving SUMMA canisters from several different manufacturers will be described in detail.

INTRODUCTION

NSI Technology Services Corporation serves a contract laboratory for the preparation of VOC audit materials for the Environmental Protection Agency. A major portion of these materials are prepared in SUMMA canisters of the same type as are used for field sampling. VOC "shelf life" is an important consideration for such canisters as they are often used as QA samples periodically during a extended period of time as well as being used immediately upon receipt. This report primarily focuses on 6 canisters loaded from the same VOC cylinder under identical conditions of humidity, etc. ; but from different manufacturers.

EXPERIMENTAL

In order to compare the stability of selected VOC's in humidified SUMMA canisters, the same Group V cylinder was selected to pressurize canisters from several manufacturers to a undiluted final pressure of 40 psig. All canisters were humidified by the injection of the appropriate amount of boiled, ultrapure deionized water to provide 50% relative humidity.

Following a 24 hour equilibration period, canisters were analyzed on a periodic basis using an HP 5890 GC/FID equipped with a cryoconcentrator and an HP-5 (crosslinked) 5% phenyl methyl silicone capillary column 30m X 0.55mm with a 0.88 um film thickness. Sample sizes were approximately the same for all analyses.

RESULTS

For simplicity, the 18 compounds present in Group V cylinders were subdivided into 4 groups according to classes of compounds and representative compound used for graphing purposes. Manufacturers are denoted by A, B, C (C1 & C2 are different types) , D, and E.

Figure 1 represents the class of compounds which includes benzene, toluene, chlorobenzene, ethylbenzene, styrene and o-xylene. Stability data is well within acceptable limits for all canisters throughout an 38 week period with the exception of A and E. Both of these canisters show a dramatic drop in concentration at 18 weeks while the others continue to show good stability.

Figure 2 represents the class of compounds which includes vinyl chloride, trichloroethylene, and tetrachloroethylene. For this class of compounds, stability is good throughout a 38 week period for all canisters except B which again shows a large decrease in concentration starting a week 20 or 21.

Figure 3 represents the compounds 1,1,1-trichloroethane, 1,2-dichloroethane, and 1,2-dibromoethane. Stability data for these compounds show a similar trend as those represented in Figure 1. A and B begin dropping in concentration at week 21.

Figure 4 represents bromomethane, freon-11, carbon tetrachloride, and chloroform. Again canisters A and B show differences from the other canisters with A dropping off at 21 weeks and B at 23 weeks.

CONCLUSION

From the results obtained, it is apparent that for up to at least 18 weeks Group V VOC's are stable regardless of who

manufactured the canisters. However, after this point in time two of the canisters show a definite concentration drop which negates their usefulness as audit materials. Thus, careful consideration of VOC residence times in humidified SUMMA canisters should be a factor in the selection of canister vendors.

ACKNOWLEDGMENTS

The authors wish to thank Shirley Henry and Annette King at NSI Technology Services Corporation for their roles in canister cleaning and preparation.

REFERENCES

- (1). This support was provided under contract number 68-02-4444 with the U.S. EPA.
- (2). For details of canister preparation and analysis procedures see last year's proceedings p.757.

FIGURE 1. AROMATIC HYDROCARBON STABILITY
Canister Manufacturer Comparisons

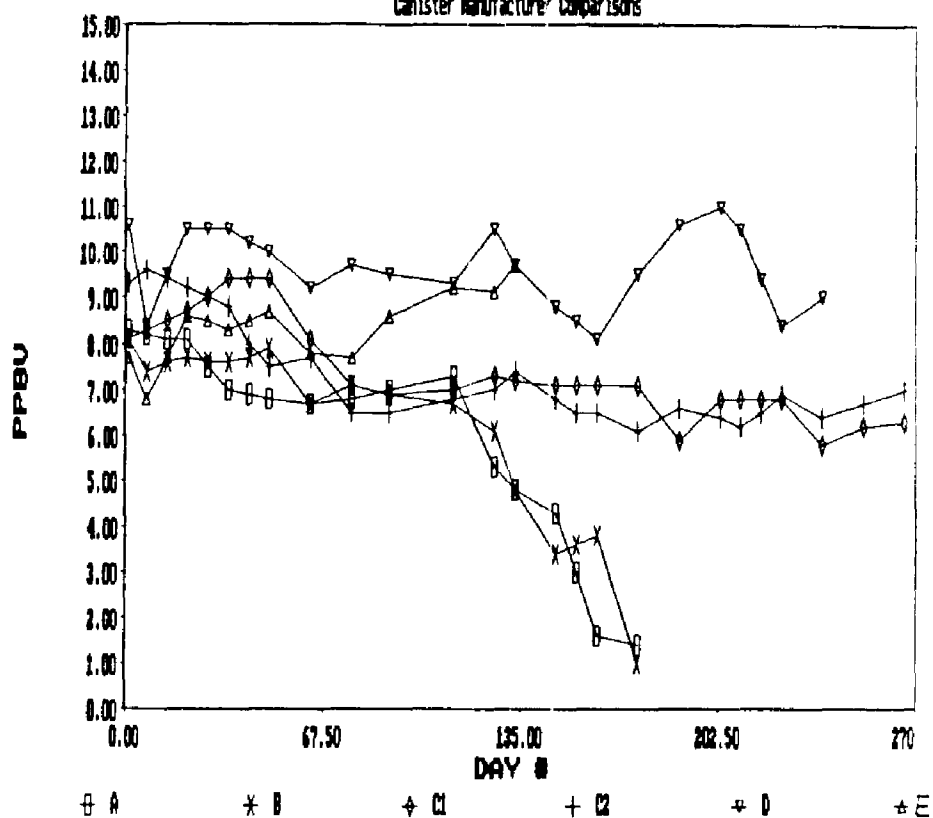


FIGURE 2. HALOGENATED ETHYLENE STABILITY
Canister Manufacturer Comparisons

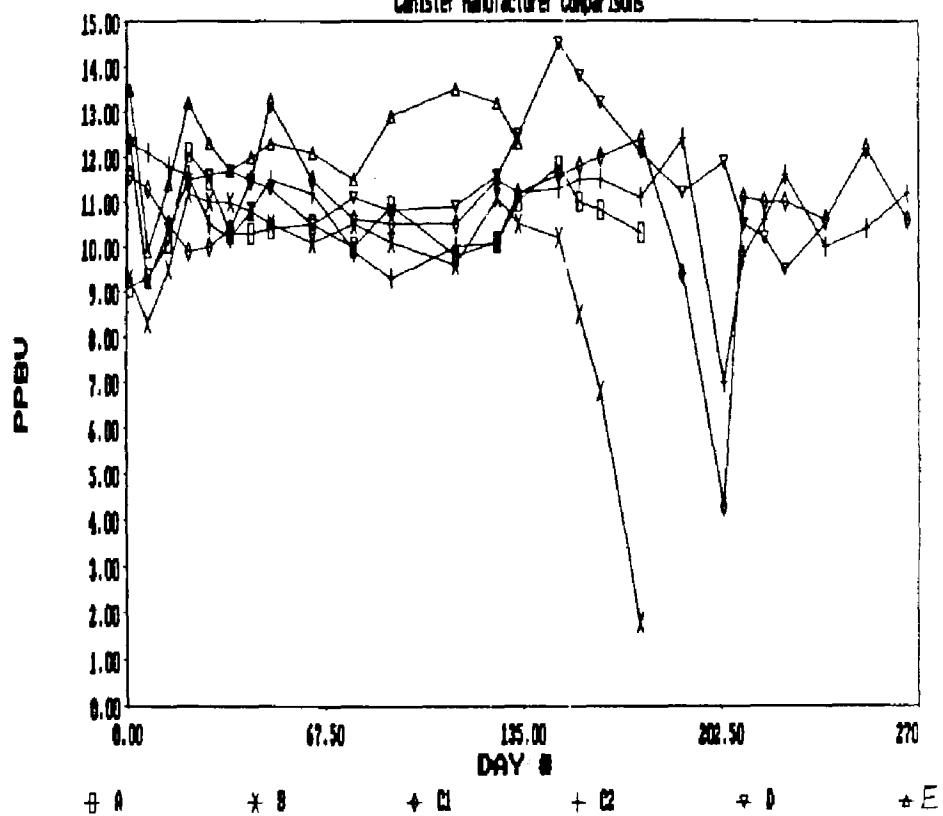


FIGURE 3. HALOGENATED ETHANE STABILITY

Canister Manufacturer Comparisons

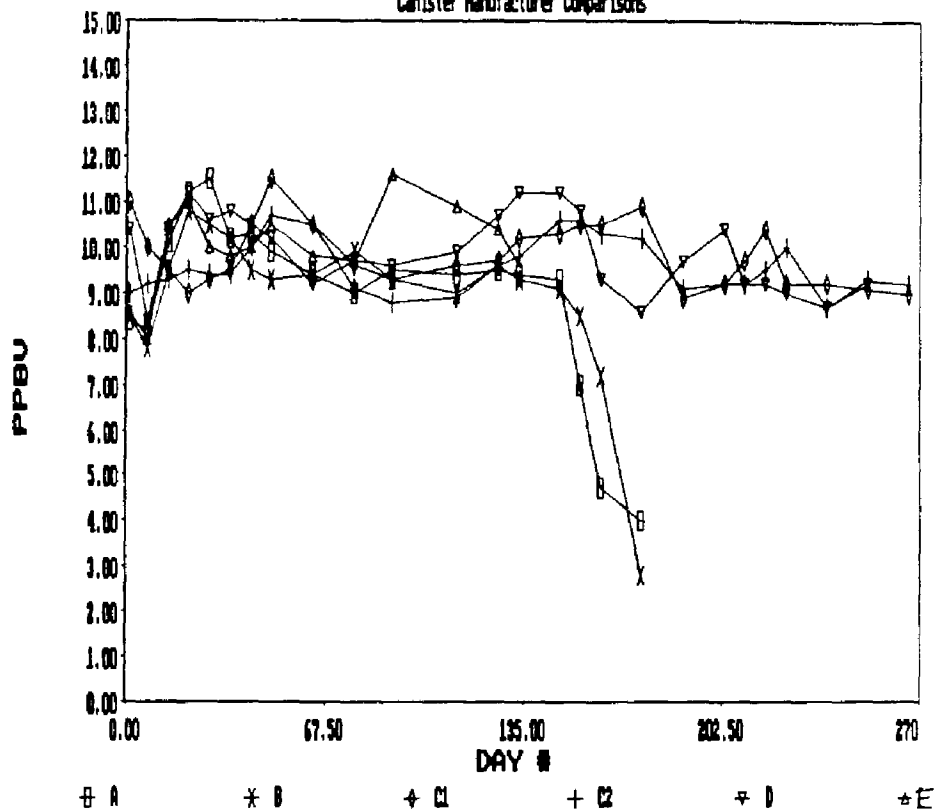
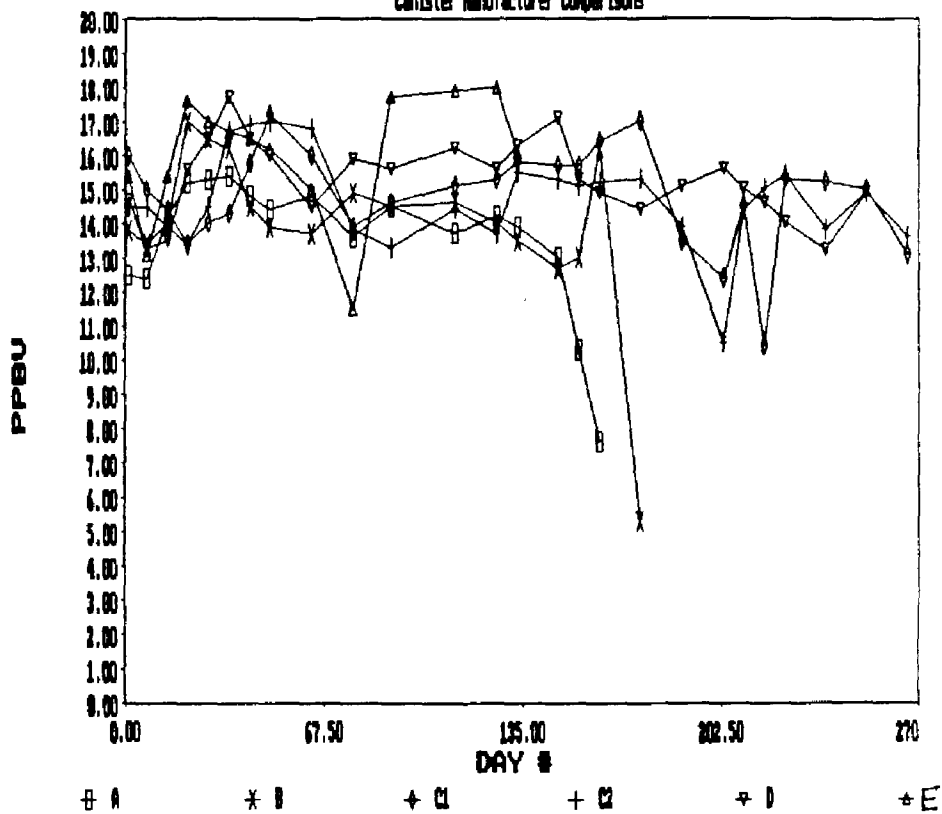


FIGURE 4. HALOGENATED METHANE STABILITY

Canister Manufacturer Comparisons



EVALUATION OF A CONTINUOUS SAMPLING AND
ANALYSIS SYSTEM FOR VOLATILE ORGANIC
COMPOUNDS

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ABSTRACT

The Louisiana Department of Environmental Quality has completed a test project on a gas chromatograph based system to collect and analyze hourly ambient air samples for Volatile Organic Compounds. Most ambient sampling strategies for Volatile Organic Compounds revolve around time integrated samples collected in canisters or on solid adsorbents. While this type of sampling strategy can provide much useful information, it cannot provide detailed data such as diurnal patterns, daily maximum/minimum concentrations, etc.

The analysis system tested is composed of a XonTech Model 930 Organic Vapor Concentrator coupled to a Hewlett Packard Model 5890 Gas Chromatograph. The sample concentrator utilizes a dual Tenax trap system which permits sample collection on one trap while an analysis is being performed on the other. The gas chromatograph is fitted with a wide bore capillary column and FID/HECD Detectors. The system is programmed to operate 24 hours per day collecting a 56 minute sample every hour with subsequent analysis. The system currently provides hourly data on 28 volatile Organic Compounds.

This paper will include a presentation of ambient monitoring data, quality assurance data, and an overall evaluation of the systems performance and reliability.

INTRODUCTION

The Louisiana Department of Environmental Quality (LDEQ) has operated an Air Toxics Monitoring Station since 1984. This station, located near downtown Baton Rouge, has been one of the few monitoring sites in the country capable of providing round-the-clock monitoring data for airborne volatile organic compounds. The original system consisted of a computer controlled dual gas chromatograph and data acquisition system. During the five years this site was in operation the analytical system was able to produce a vast amount of monitoring data. However the site was also besieged with a number of problems. These problems included compound misidentification due to low chromatographic resolution, high maintenance costs, frequent breakdowns, and an inadequate data system. During the spring of 1989 a search began for a replacement system.

In order meet the goals of the LDEQ AIR Toxics monitoring program and address the problems experienced with the existing monitoring station the new equipment selected had to meet several requirements.

- Hourly Samples of at least 56 minute duration
- Concentrator must start GC and Data System
- Dual bed sorbent traps to enable capture C2-C10 hydrocarbons
- Dual detectors:
 - Flame Ionization Detector
 - Electrolytic Conductivity Detector (Halogen mode)
- Detection levels down to 0.1 ppbv for selected compounds
- User selectable sample, zero, and calibration analyses
- Data reports at the end of each hourly run
- Storage of data in PC compatible files
- Ability to recover after a power failure

In addition to the above requirements the replacement system had to be cost effective by providing a high volume of data with low costs for operation and maintenance.

SYSTEM DESCRIPTION

In July of 1989 the replacement system was selected and placed into operation. This system consists of the following three sub-systems;

1. XonTech Model 930 Organic Vapor Concentrator equipped with dual sorbent bed traps.

2. Hewlett Packard 5890 gas chromatograph equipped with a Flame Ionization Detector & an O.I. Electrolytic Conductivity Detector configured in the halogen mode.

3. Dual Hewlett Packard Model 3396 programmable computing integrators equipped with HP-BASIC.

In addition a GRID lap top MS-DOS computer was purchased in order to extract the data from the integrators and transfer it to the agency database.

The XonTech model 930 Organic Vapor Concentrator consists of two vertically mounted sorption traps which are alternately activated in order to provide continuous air sampling. The traps consist of a 1/8" o.d. x 12" long stainless steel tube packed with a 6" bed of Tenax TA backed up with a 3" bed of Carboxen-564. This type of dual bed trap has been shown to provide excellent recoveries for a wide range of compounds. The sample flow rate is set at 10 CC/min providing a total sample volume of 560 CC. Each trap is heated and cooled separately for independent operation through the following 60 minute cycles:

- A. 56.0 minute sampling of ambient air
4.0 minute Helium purge to remove air from sorbent tube
- B. 2.5 minute Desorption at 200°C to inject sample
15.0 minute cleaning at 215°C
42.5 minute cooling to ambient temperature

During continuous operation when one trap is performing cycle A, the other trap is performing cycle B. At the end of the 60 minute cycle the traps switch functions. At the beginning of each desorption cycle the concentrator sends a remote start signal to the GC and the integrator data system. The Organic Vapor Concentrator is connected to the Gas Chromatograph by means of a heated transfer line.

The gas chromatograph is equipped with a sample splitter that divides the sample between two separate columns. A SPB-1 capillary column 50 m x 0.53 mm x 2.65 μ m is attached to the Flame Ionization Detector while a SPB-1 column 25 m x 0.32 mm x 0.52 μ m is attached to the Electrolytic Conductivity Detector. This combination yields a split ratio of about 5:1 in favor of the FID. The GC is temperature programmed for an initial temperature of 30 degrees C. Three minutes after the run start the temperature is increased at a rate of 2.5 degrees C per minute up to a final temperature of 130 degrees C. The total GC run-time is 45 minutes.

The monitoring system is calibrated three times a week using compressed gas cylinders containing certified concentrations of the compounds of interest. The retention time of each compound is stored in the integrators along with an appropriate specific response factor. At the end of each subsequent analysis the integrators automatically execute a BASIC program which matches retention times to identify compounds and quantifies them by using the specific response factors determined during the calibration analyses. The total areas of all peaks including unknowns are summed for each detector. Total area on the Flame Ionization Detector is multiplied by the hexane response factor to yield a value for total hydrocarbons. Total area on the Electrolytic Conductivity Detector is multiplied by the ethylene dichloride response factor to yield a value for total chlorinated VOC. The data is then written to a daily data file in each integrator and stored under unique file names. At midnight each day a 24 hour summary report is printed. Each integrator has enough memory capacity to hold at least six days of data. Periodically the site operator will transfer the data files from the integrators to the lap top computer for editing and subsequent storage in the agency database.

In addition to the analytical data, the monitoring site has a meteorological equipment tower which measures wind direction, wind speed, and ambient temperature. This data is gathered in the form of hourly averages and stored in the agency database along with each chromatographic analysis.

Detection levels have been determined to be about 0.1 ppbv on the Flame Ionization Detector for most of the hydrocarbons and about 0.02 ppbv on the Electrolytic Conductivity Detector for the chlorinated VOC.

OPERATIONAL RESULTS

Since the monitoring system was placed in operation it has been able to sample and analyze around 700 ambient air samples per month. The equipment has been able to recover from most short term power failures resulting in little loss of data. There were a few problems initially with background noise on the Electrolytic Conductivity Detector. Once that problem was solved both detectors have subsequently performed quite well.

The monitoring system was subjected to several tests in order to fully evaluate the precision and accuracy. A performance audit cylinder containing low ppbv levels of several volatile organic compounds was attached to the sampling manifold and subsequently analyzed. The results listed in (Table 1)

show the monitoring system was able to measure most of the compounds within an accuracy of $\pm 20\%$. In order to evaluate the precision and repeatability of the system, a gas mixture was sampled repeatedly over a eight hour period. The results show a slight difference ($\pm 5\%$) in instrument response occurring on alternating runs. This effect is caused by slight differences in the trapping and/or desorption efficiency between the two sorbent traps. Since the concentrator unit has the capability of injecting an internal standard with each sample, it is felt that the use of an internal standard calibration method will eliminate this minor problem.

The monitoring system was co-located with a canister based, time integrated sampling system which was part of the Urban Air Toxics Monitoring Program. A comparison of data was made by taking the mean average of the 24 hourly samples on a given sample date, and comparing those averages to the results obtained from the canister analysis. The results contained in (Table 2) show the monitoring system is capable of producing data of nearly the same quality as the time integrated canister based sampling system.

AMBIENT DATA RESULTS

Table 3 shows the mean average concentrations observed for the period January 1, 1990 through March 31, 1990. During this period of time the monitoring system collected and analyzed 2003 samples. This represents a data capture of 92.7%.

The most striking fact about the monitoring data gathered is that the levels of volatile organic compounds observed are highly variable. Often during any given twenty four-hour period the range of measured concentrations can be quite high. The diurnal pattern of concentrations can be observed by sorting the monitoring data by the hour of the day in which the samples were collected. As a result it can be seen that most of the hydrocarbons generally reach their maximum concentrations during the 6 - 9 am period and hit their lowest reading during the 12 - 3 pm period (Figure 2). No noticeable diurnal pattern was observed for the chlorinated volatile organic compounds.

Another useful type of data analysis involves sorting the data into groups according to the direction from which the wind was blowing when the samples were collected. This kind of data analysis is valuable in pinpointing the effect local point sources can have on a monitoring station. The LDEQ monitoring station is located to the south of several petrochemical plants. Consequently when the wind is from a northerly direction a corresponding increase in the observed levels of volatile

organic compounds can be seen (Figure 3).

CONCLUSIONS

The continuous monitoring system established by LDEQ provides a useful alternative to the field collection and laboratory analysis of ambient air samples. Initial estimates of the precision and accuracy compare favorably with the precision and accuracy measured during the early development of other air toxics monitoring techniques. Improvements in the precision and accuracy are expected as the knowledge and understanding of the system operation grows. The overall performance of the system has been good enough that LDEQ has begun formulating plans to expand this type of monitoring program to several sites around the state.

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TABLE I

Performance Audit Results

RTI Cylinder AAL-21515

Compound	RTI Conc. PPB	DEQ Analysis PPB	
vinyl chloride	5.27	3.21	-39.1%
methylene chloride	4.41	3.74	-15.3%
chloroform	4.85	4.88	+ 0.3%
1,2-dichloroethane	5.06	4.43	-12.5%
carbon tetrachloride	5.06	4.75	- 6.2%
trichloroethylene	5.10	4.55	-10.8%
perchloroethylene	5.24	5.09	- 2.8%
benzene	5.59	5.42	- 2.9%
toluene	5.19	5.04	- 2.9%
ethyl benzene	4.80	4.81	+ 0.3%
o-xylene	5.29	5.00	- 5.5%

TABLE II

Data Comparison with Canister Based Sampler

Date of Sample	Benzene		Toluene	
	LDEQ - Canister		LDEQ - Canister	
7/27/89	1.7	- 1.60	2.4	- 2.51
8/08/89	2.1	- 2.12	3.1	- 2.30
8/20/89	2.2	- 2.13	3.7	- 2.55
9/01/89	0.6	- 0.68	1.0	- 0.95
9/13/89	1.2	- 1.12	2.5	- 2.14
9/25/89	1.3	- 0.79	1.1	- 0.88

Concentrations in PPBV

(TABLE 3)

AVERAGE CONCENTRATIONS MEASURED

FID HYDROCARBONS - BATON ROUGE, LA.

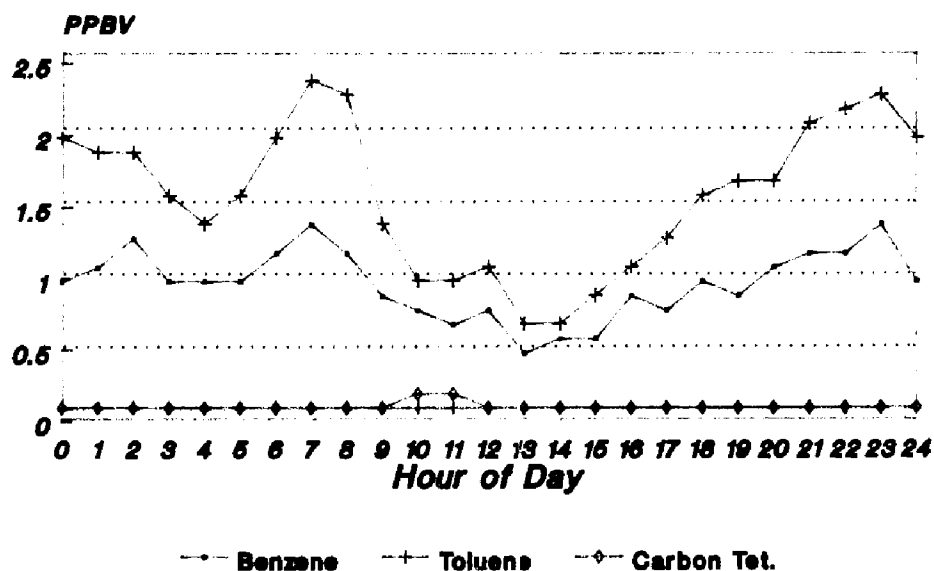
<u>Compound</u>	<u>Mean Average Concentration (PPBV)</u>
Propane	8.4
Butane	4.7
2-methylbutane	3.7
Pentane	1.9
2-methylpentane	1.0
3-methylpentane	0.6
Hexane	1.0
Methylcyclopentane	0.5
Benzene	1.0
2-methylhexane	0.2
2,2,4-trimethylpentane	0.3
Heptane	0.2
Methylcyclohexane	0.2
Toluene	1.6
Octane	0.1
Ethylbenzene	0.2
m+p xylene	1.3
o xylene	0.6
Cumene	0.2
1,2,4-trimethylbenzene	1.2
Unknowns	6.3
Total Hydrocarbons	35.2

ELCD CHLORINATED VOC - BATON ROUGE, LA.

<u>Compound</u>	<u>Mean Average Concentration (PPBV)</u>
Vinyl Chloride	0.4
Methylene Chloride	0.1
Chloroform	<0.1
Ethylene Dichloride	0.5
Carbon Tetrachloride	0.1
Trichloroethylene	<0.1
Perchloroethylene	0.1
Unknowns	1.5
Total Chlorinated VOC	2.5

FIGURE I

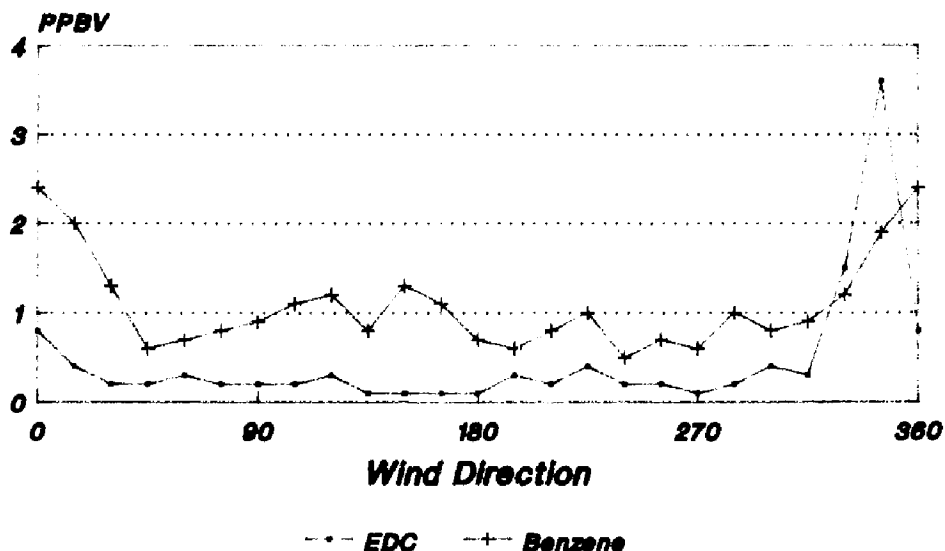
Diurnal Variation in Concentration Baton Rouge, Louisiana



January 1, 1990 - March 31, 1990

FIGURE II

Variation of Concentration with Change in Wind Direction



January 1, 1990 - March 31, 1990

CANISTER BASED SAMPLING SYSTEMS - A PERFORMANCE EVALUATION

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Canister based sampling systems have gained wide acceptance for the collection of integrated whole ambient air samples containing volatile organic compounds. Utilization of this sample collection method has increased significantly. There are many different canister based sampling systems. The various sampling system incorporate diverse operating principles but always share one common element, a SUMMA®-treated, stainless steel canister as the sample containment vessel. The technique and associated hardware used to time-integrate the sample is the primary difference between the various operating principles. Integration techniques include the use of several electronic and/or mechanical devices. These devices include pumps, variable orifices, fixed orifices, and mass flow controllers, either separately or in combination. Radian Corporation has designed, fabricated, and used canister based sampling systems, encompassing many of the various operating principles, during several large field sampling programs. A performance evaluation of several canister based sampling systems, addressing time-integration characteristics and reliability has been compiled. An estimate of sampler system associated bias is assessed, based on the suggested certification procedure detailed in Method TO-14, published by the U.S. Environmental Protection Agency.

INTRODUCTION

Canister based sampling systems have gained wide acceptance for the collection of time-integrated whole ambient air samples containing volatile organic compounds. There are many canister based sampling systems which incorporate diverse operating principles but always share one common element, a stainless steel SUMMA®-treated canister as the sample containment vessel.

The technique and associated hardware used to perform time-integration of a canister sample is the primary difference among the various operating principles. Time-integration techniques generally involve the use of electronic and mechanical devices either separately or in combination. Several of these systems are commercially available while others are custom built for a specific application.

Radian Corporation has gained vast experience with canister based sampling systems through the management and operation of the multiyear national Nonmethane Organic Compound (NMOC) and Urban Air Toxics Monitoring Program (UATMP), under contract to the U.S. Environmental Protection Agency (U.S. EPA). Radian Corporation has also managed and operated extensive regional monitoring networks for private industry. The operation of these government and industry monitoring networks has involved the design, fabrication, certification, deployment, and operation of approximately 100 canister sampling systems encompassing many of the current principles of operation. Modification and repair of the sampling systems are also an integral part of operating the monitoring networks. During the course of these programs approximately 14,725 samples were collected at over 218 sites across the country during the past six years.

The following performance evaluation of canister sampling systems is based on experience gained during the aforementioned programs. The evaluation addresses system associated bias, based on the certification procedure suggested in Method TO-14.¹ In addition, time-integration characteristics and reliability are assessed.

SAMPLING SYSTEM GROUPING

Although the evaluated sampling systems incorporated various operating principles, they can be categorized into three basic groups. Systems in Group A use negative pressure generated by a pump pulling against an orifice assembly to deliver an integrated sample into the canister. Group A sampling systems can be used to collect a sample that has either a negative or a positive final pressure. This is usually dependent upon the needs of the analytical methodology for which the sample is being collected. This paper addresses only negative final sample pressure collections. Systems in Group B use an electronic mass flow controller and the vacuum present in the canister to deliver a time-integrated sample into the canister. Systems in Group C use the vacuum present in the canister pulling against a vacuum regulation assembly to deliver an integrated sample into the canister.

Group B and C systems can be used to collect negative final pressure samples only, unless a pump is also incorporated into the sampling system. None of the models of mass flow controlled or vacuum regulation sampling systems evaluated incorporated a pump.

SAMPLING SYSTEM CERTIFICATION

Procedure

Sampling systems are subjected to a laboratory certification procedure to quantify any additive or subtractive biases the sampling systems may contribute to the samples they collect. The certification procedure, described in Method TO-14,¹ involves determination of system specific compound recovery and contamination. A challenge sample of a blend of organic compounds at known concentrations in humidified air, is collected through the sampling system. Analysis of the challenge sample is performed and percent recoveries of the organic compounds are calculated. The calculated percent recoveries are used as a gauge of additive and/or subtractive bias on a system specific basis. A humidified zero air blank sample is then collected through the sampling systems to gauge further additive bias.

Results

Twenty-two Group A sampling systems, representing three different models, received sampler certification. The three models included in Group A were the U.S. EPA NMOC Sampler, the Radian Corporation RCS Sampler, and the Scientific Instrumentation Specialists AGS-1/B Sampler. Thirty-four Group B sampling systems, representing three different models, also received sampler certification. The three models included in Group B were the U.S. EPA UATMP Sampler, the U.S. EPA Modified Type "L" Sampler, and the Radian Corporation RCS/M Sampler. Four Group C sampling systems, representing one model, received sampler certification. The model included in Group C was a Veriflow Vacuum Regulator. A blend of benzene, methylene chloride, toluene, vinyl chloride, and o-xylene, all at approximately 104 ppbv, was delivered to the Radian Certification System from a high pressure cylinder. Humidified zero air from the Radian Canister Cleaning System was also delivered to the certification system and mixed with the organic compounds to produce the desired challenge sample concentrations.

Each of the Group A and Group B sampling systems collected a challenge sample from the Radian Certification System. The challenge samples were analyzed by multiple detector gas chromatograph and percent recovery for each compound tested was calculated on a sampler-specific basis. The individual percent recovery figures were then averaged on a compound-specific basis within the two sampling system categories. Table 1 presents the sampling systems challenge data. Average recoveries calculated for the Group A systems ranged from 94.8% for o-xylene to 108.7% for toluene, with an overall mean of 102.8 percent. Standard deviations for the Group A systems ranged from 2.6% for methylene chloride to 7.7% for toluene, with an overall mean standard deviation of 4.5 percent. Average recoveries calculated for the Group B systems ranged from 80.2% for vinyl chloride to 100.9% for o-xylene, with an overall mean of 91.7 percent. Standard deviations for the Group B systems ranged from 2.1% for o-xylene to 22.2% for vinyl chloride, with an overall mean standard deviation of 11.2 percent. Average recoveries calculated for the Group C systems ranged from 91.7% for benzene to 108.0% for o-xylene, with an overall mean of 98.2 percent. Standard deviations for the Group C systems ranged from 1.8% for methylene chloride to 15.9% for o-xylene, with an overall mean of 10.7 percent. Comparing the means of the percent recoveries for the challenge samples shows there is an apparent difference at the 0.05 level of significance or a 95% probability between the Group A sampling systems and the Group B systems. There is also an apparent difference between Group A sampling systems and Group C systems. There is no apparent difference between Group B sampling systems and Group C systems. Not enough data is currently available to explain these differences. Although there is a statistical difference between the Group A and Group B and C recovery data, 92%, 103%, and 98% are generally considered to be reasonable and acceptable percent recoveries.

When the collection of the challenge samples was completed, all the sampling systems were purged for 48 hours with zero air that had been humidified to 80% relative humidity in preparation for the system blank sample collections. The purpose of the system blank samples is to assess sampler cleanliness as a further gauge of additive bias. It is not a test of sample carryover. The acceptance criterion for sampling system cleanliness, as described in Method TO-14,¹ is less than 0.2 ppbv of any target compound analytes. After the 48-hour purge, each of Group A, Group B, and Group C sampling systems collected a system blank sample. The system blank samples were analyzed by multiple detector gas chromatography.

Ninety-one percent of the Group A systems and 75% of the Group C systems were able to meet the acceptance criterion after 48 hours of purge, while only 32% of the Group B systems were able to meet the criterion. This is not to say that the Group A and Group C systems are inherently cleaner, but rather that they can be cleaned faster. It is theorized, that this is due to the ability of the Group A and Group C systems to operate at a higher flow rate, typically 3 to 5 L/minute. The highest flowrate for the Group B systems is dictated by the range of the mass flow controller being utilized, typically 20 to 100 mL/minute. Invariably, all the sampling systems were able to meet the cleanliness criterion with additional purging. The maximum additional purge time required was 48 hours.

An area that has been lacking in most canister sampling network programs is a method of performing some form of certification in the field, using humidified standards and humidified zero air. This in-the-field certification is recommended to be performed on a regular schedule throughout the period of

performance of the sampling effort and would, in fact, serve as a performance audit. Regularly administered audits would give insight into compound recovery variability and sample carryover. The U.S. EPA is developing a trial in-the-field canister sampling system audit procedure that will be evaluated during the 1990 Urban Air Toxics Monitoring Program.²

SAMPLING SYSTEM TIME-INTEGRATION CHARACTERIZATION

Procedure

A time-integrated canister sample is defined as a sample that is collected at a constant flowrate throughout the sample collection period. If the collection flowrate varies during the collection period, the sample could be biased or not representative of the ambient air sampled, assuming the concentration of compounds present in the ambient air changes throughout the sampling period.

To perform time-integration characterizations, a system incorporating a calibrated mass flow meter and a strip chart recorder was used to measure any flowrate deviations that occurred during varied sampling conditions. The sampling system being characterized pulled humidified zero air through the calibrated mass flow meter and delivered it to the sample canister at a preset collection flowrate. The electronic output from the mass flow meter was recorded by the strip chart recorder, and a real-time assessment of flowrate variation was made. An absolute pressure gauge was plumbed into the outlet transfer line between the sampling system and the sample canister. This allowed for the real-time assessment of pressure change within the sample canister in relation to the sample flowrate.

Results

Group A, Group B, and Group C sampling systems were setup to collect 24-hour samples of humidified zero air, through the time-integration assessment apparatus. Collection flowrates of 3.6 mL/min for the Group A systems and 3.3 mL/min for the Group B systems were used. These collection flowrates were determined to yield time-integrated samples with negative final sample pressures in evacuated six-Liter SUMMA®-treated canisters. The initial average measured pressure in the 6-L canisters was 29.92 inches Hg vacuum.

A collection flowrate of 5.6 mL/min was used for the Group C systems. This flowrate represents the extreme lower end of the range of flow attainable with the Veriflow Vacuum Regulators. This collection flowrate was determined to yield a time-integrated sample with a negative final sample pressure in evacuated 15L SUMMA®-treated canisters. The initial average measured pressure in the 15L canisters was 29.78 inches Hg vacuum.

The Group A systems displayed very good time-integration characteristics during the 24-hour, negative final sample pressure collections. They maintained a constant flowrate as long as the sample canister pressure remained negative. Group A systems set for an average sample flowrate of 3.6 mL/min maintained this flowrate during the 24-hour test period with no measurable flowrate change. The final measured sample pressure averaged 3.73 inches Hg vacuum. This represents approximately 87% of the 6-L canister volume replaced with sample.

The Group B systems evaluated displayed very good time-integration characteristics during the 24-hour, negative final sample pressure collections. Group B systems set for an average collection flowrate of 3.3 mL/min maintained this flowrate during the 24-hour test period with no measurable flowrate change. The final measured sample pressure averaged 6.1 inches Hg vacuum. This represents 79% of the canister volume replaced with sample.

A pressure differential across mass flow controllers is required to enable them to maintain a set flowrate. The pressure difference required varies from model to model and also unit to unit within the same model type. The average required pressure difference observed during the Group B evaluation was 1.8 inches Hg vacuum. Mass flow controllers intended for use in a vacuum mode should receive a negative

pressure calibration instead of the positive pressure calibration that is normally standard from most manufacturers.

The Group C systems evaluated displayed good time-integration characteristics during the 24-hour, negative final sample pressure collections. Group C systems set for an average collection flowrate of 5.6 mL/min., maintained this flowrate during the 24-hour test period with no measurable flowrate change. The final measured sample pressure averaged 12.1 inches Hg vacuum. This represents 54% of the canister volume replaced with sample.

A pressure differential across vacuum regulators is required to enable them to maintain a set flowrate. The pressure difference required varies from model to model and also unit to unit within the same model. The average required pressure difference observed during the Group C evaluation was 12.1 inches Hg vacuum.

Once an individual sampling systems time-integration characteristics are determined, they can be used as a quality control measure. Any specific sampling system operated at the same collection flowrate repeatedly should yield the same approximate final sample pressure repeatedly. Any deviation in final sample pressure greater than 15% is an indication that something abnormal occurred which could impact sample validity.

SAMPLING SYSTEM RELIABILITY

In general, both Group A and Group B sampling systems operate reliably. Since 1984, Radian Corporation has collected or overseen the collection of approximately 13,609 samples using 68 Group A systems at approximately 179 sites across the country. Valid sample collections using the Group A systems occurred at an average rate of 93.4 percent. Radian Corporation has also collected or overseen the collection of approximately 1116 samples using 27 Group B systems at approximately 40 sites across the country. Valid sample collections using the Group B systems occurred at an average rate of 95.0 percent. The reliability of Group C systems was not assessed because they are normally activated and deactivated manually.

The sampling systems have proven to be mechanically durable. Procedural misoperation of the sampling systems by the site operators account for the bulk of failed sample collections. Mechanical failures account for only one-third of the 5.8% of failed collections. The majority of the mechanical problems involved improper activation or deactivation of the latching solenoid valves, pump failures, or system leaks. Leaks are considered to be a mechanical problem because they are usually caused by the vibration set up by the sampling and/or slipstream by-pass pump incorporated into systems. Improper operation of the sampling systems by site operators accounted for the remaining two-thirds of unsuccessful sample collections. The primary procedural problems causing unsuccessful sample collection were improper programming of the sampling system activation/deactivation timing device and failure of the operator to open or close the sample canister bellows valve either prior to or after sample collection.

CONCLUSIONS

When operated properly, Group A, Group B and Group C canister based sampling systems offer a reliable method for the collect of representative whole ambient air samples containing volatile organic compounds. They exhibit good compound recovery characteristics for the compounds tested. They are acceptably nonbiasing. The area of sample carryover has not been researched in depth. More data to quantify sample carryover needs to be obtained. The sampling systems will perform time-integrated sample collections when operated within sampler specific parameters. Sampler specific time-integration characteristics can be used as a quality control measure to gauge sample validity. Successful sample collection using the sampling systems described averaged 94.2%, with most of the failures attributed to improper operation by the system operators. The Group C systems offer a viable sampling approach in applications where sources of electric power are not available or to accommodate cost considerations.

There was no apparent overwhelming advantages in reliability, certifiability or time-integration characteristics between Group A and Group B systems. The amount of vacuum remaining in a sample

canister at the end of a Group C collection and the inability of Group C systems to use 6L canisters is a disadvantage. Although not specifically addressed in this paper, there is also no clear advantage in initial cost or cost to operate between pumped and mass flow controlled sampling systems.

ACKNOWLEDGEMENTS

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TABLE I. SAMPLING SYSTEM CHALLENGE RESULTS

Compound	\bar{X} Concentration (ppbv)	Group A Systems			Group B Systems			Group C Systems		
		Cases	\bar{X} % Recovery	Standard Deviation	Cases	\bar{X} % Recovery	Standard Deviation	Cases	\bar{X} % Recovery	Standard Deviation
Benzene	12.7	22	104.0	3.7	34	94.5	5.3	4	91.7	12.9
Methylene chloride	13.4	22	101.5	2.6	34	91.2	18.6	4	102.7	1.8
Toluene	12.4	22	108.7	7.7	34	91.5	7.7	4	90.4	14.0
Vinyl chloride	12.9	22	104.8	5.4	34	80.2	22.1	4	98.1	9.1
o-Xylene	<u>13.7</u>	22	<u>94.8</u>	<u>3.3</u>	34	<u>100.9</u>	<u>2.1</u>	4	<u>108.0</u>	<u>15.9</u>
Mean	13.0		102.8	4.5		91.66	11.2		98.2	10.7

**MOBILE AMBIENT AIR SAMPLING AND ANALYSIS
EXPERIENCE OF THE TEXAS AIR CONTROL BOARD**

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The content of this presentation will summarize the Texas Air Control Board's (TACB) past experience in sampling and analyzing the ambient air for organic compounds in the vicinity of chemical and petrochemical complexes. The basis for and the philosophies of the sampling conducted, area and focused, will be discussed.

The techniques and methods used for collecting and analyzing ambient air samples will be discussed. The presentation will include "real-time" methods and those which use a variety of solid absorbents. The TACB's thermal desorption experience using carbon molecular sieves will be emphasized.

The process, from conception to final results of conducting a week-long and intensive mobile sampling effort, will be presented in detail. This presentation will include duplicate and audit results of the techniques used by the TACB in ambient air analyses.

Introduction

The Texas Air Control Board (TACB) is the state regulatory agency whose legislative mandate is to protect the ambient air resources of the State of Texas. The TACB operates under the Texas Clean Air Act. TACB rules and regulations are aimed at maintaining an ambient air environment that is not a detriment to the welfare of the general public. Monitoring the ambient air is one of the ways that the TACB can provide the general public with information concerning the quality of the ambient air environment to which they are exposed. Other means of controlling the ambient air are through the permitting process and regular in-plant inspections conducted by TACB staff. TACB regional investigators routinely collect ambient air samples in areas of concern to them and in response to citizen concerns and complaints. These samples are then analyzed by the central office laboratory. Such sampling and analysis often generates information which will result in a request for intensified ambient air sampling in an area of concern. Upon management approval, the Sampling and Analysis Division of the TACB will plan, coordinate and conduct five days of intensified sampling and analysis for potential organic ambient air pollutants using its mobile analytical capabilities. It is the experiences of the mobile capability that this document will describe.

Initial Efforts (305)

The TACB began mobile sampling in the late 1970's. The early efforts were conducted using a van outfitted with one or more gas chromatographs (GC) equipped with flame ionization detectors and selective detectors. In-the-field electrical power was provided by a gasoline-powered electrical generator. On occasion, sampling was conducted using instrumentation to detect sulfur dioxide and hydrogen sulfide. The sampling done with these capabilities were point source oriented. Generally, only one or two compounds were sought and selective GC detectors and retention times were depended upon for identification. These early efforts generated the ideas that led to the mobile laboratory capabilities that the TACB now possesses.

Mobile Laboratory Endeavors

A decision to initiate a mobile laboratory trip is usually based on information supplied by regional investigators or upon ambient air modeling of a point source by TACB engineers. The Sampling and Analysis Division, in consultation with Regional, Enforcement, Permitting and Health Effects personnel, select the sampling sites and compounds to be targeted during the sampling trip. Early mobile laboratory trips could be described as those which involved "area sampling." In these instances, sampling was conducted around chemical complexes and in the adjacent neighborhoods with a "what's there and how much" approach. Financial and manpower resources have directed our mobile laboratory trips to a "focused sampling" concept. In the focused sampling concept, emission inventories are reviewed, individual compounds are prioritized based on their potential to cause adverse health effects and the sampling and analytical effort is designed to detect and quantify a target list of compounds.

Mobile Laboratory. The TACB mobile laboratory is a 40-foot trailer that has been outfitted to accept instrumentation necessary to accomplish the proposed sampling and analytical effort in an area of concern. A gas chromatograph/ion trap detector (GC/ITD) is permanently mounted in the trailer. A fume hood and a glove box were initially installed because the type of sampling media being used required chemical desorption of the adsorbed air contaminants.

Historically, during these endeavors of intensified sampling, the samples were collected on gram quantities of activated purified charcoal using modified high-volume air samplers. Occasionally, other media would be placed after (before) the charcoal in order to produce a specialized collection technique. Generally, these samples were collected over a ten to 12 hour period. For short-time samples of one to three hours, OSHA-type charcoal tubes were employed. Methanol, methylene chloride, carbon disulfide and/or tetrahydrofuran were used as solvents to release the air contaminants from the adsorbing media. Thus, the fume hood and glove box were welcome accessories to the mobile laboratory.

The majority of the mobile sampling endeavors undertaken by the TACB have been near the coastline of Texas where relative humidities are frequently high. Experienced samplers and analysts can appreciate the problems that were encountered using activated charcoal as an adsorbing media. Moisture can preclude the adsorbance of air contaminants on activated charcoal. Moisture can also impede the chemical desorption of adsorbed contaminants by not being soluble in the desorbing chemical solvent. TACB analysts have experienced conditions where it was necessary to chemically desorb the activated charcoal with two solvents, analyze both extractions by GC/ITD, and sum the results without being confident that the adsorbed air contaminants had been efficiently recovered, due to the effects high humidity can produce.

Current Procedures

For a year and one-half, the TACB has been using carbon molecular sieve (CMS) tubes to collect ambient air samples. Subsequent analysis involves thermal desorption of the collected contaminants onto a sub-ambient fused silica capillary column.

Collection of the samples is accomplished using an SKC Model 224-PCXR7 pump. This pump has the capability of continuous or intermittent operation, and can be programmed to sample a set volume of ambient air over a time period of up to one week. The adsorbing media is Supelco's carbotrap 300 tube, which consists of carbotrap C/Carbotrap/Carbosieve III. This adsorbent is purported to work well with U.S. Environmental Protection Agency TO-1, TO-2 and TO-3 methodology. Our experience has shown that retaining 1,2-butadiene is a problem at parts per billion (ppb) concentrations. Fifty percent of the 1,3-butadiene will "self desorb" in the first 24 hours and is not detectable after 48 hours of storage when working with ppb concentrations. In addition, attempts to use the CMS tube to collect sulfur-containing compounds has not been productive.

Thermal desorption is accomplished using a Dynatherm Model 850 tube desorber. Chromatography is usually accomplished using a DB-1 or DB-5 column, 30 meters in length, contained in a Varian 3400 GC. Identification and quantitation of the individual eluting compounds is accomplished with a Finnigan Model 800 ITD.

Typically, the thermal desorption is done at 325°C. The analytical column is held at -25°C for four minutes. It is then temperature-programmed at 50°C/minute to 50°C and then at 10°C/minute to 250°C. Helium is used as the carrier gas, flowing through the CMS sample tube at seven cc/minute. Two cc or less of this total flow is split to the analytical column for analysis. Internal diameter and length of the analytical column will determine the upper limit of flow to the analytical column. Sampling only four liters of ambient air provides sufficient sample for the analytical scheme described here. With the ITD in full scan mode, 500 pptv of most of the compounds of interest are routinely identified and quantified.

Those of you who are familiar with the thermal desorption process have probably already noted several things in this analytical scheme. First, there is no re-focusing of the sample onto a second adsorber bed and there is no cryofocusing device. The whole column is held sub-ambient. Admittedly, the front end chromatography does not develop sharp peaks for the earlier eluting compounds. Fortunately, to date there have been few compounds of interest to the TACB eluting in that portion of the chromatogram. Secondly, there is no flushing of the CMS sample tube to remove potentially collected water. The CMS tubes are advertised to be hydrophobic. If water is retained by the CMS tubes, the quantity is such that there has been no observed adverse effects in the operation of the ITD.

When in the field, the mobile laboratory serves as the base of operations and support for the other sampling vans. Sampling is conducted 24 hours a day by two 12-hour shifts. Sampling begins on a Saturday evening and continues until the following Friday morning. During this time frame, 90-100 CMS tubes will be used to collect three-hour composite samples. In addition, approximately 1200 real-time samples will be analyzed. The analysis of the CMS tubes is accomplished using the mobile laboratory ITD and a second ITD temporarily mounted in a sampling van.

Typical field operations have the mobile laboratory with its ITD and a real-time GC. Wind speed and direction are monitored at the mobile laboratory. A van with one or two GC's and the second GC/ITD travel to appropriate sampling sites for the collection of composite samples and real-time samples in addition to analyzing CMS tubes by GC/ITD. A second van will be outfitted with one or two GC's, as appropriate, and travels to sampling sites to collect real-time samples and composite samples on CMS tubes. A third van is deployed to collect only composite samples.

Real-time sampling provided an interesting observation during a recent sampling trip. Winds had been southeasterly for two to three days from a source of styrene. Due to a cold front, the wind changed 180 degrees. The observed level of styrene from real-time sampling remained constant for eight-ten hours. During the next four-six hours, the observed styrene concentrations went to a non-detectable level. This would infer that under the proper meteorological conditions that "a cloud of pollutant" could move in one direction, only to return with a reversal of wind direction.

The focused approach type of sampling attempts to collect the highest concentration that a point source is emitting to the ambient air. Location of the samplers in relation to the emission source under a given set of meteorological conditions is very important, especially when the compound being sought has little or no odor at sub-ppm levels. The importance of sampler location was observed during a sampling exercise for 1,2-dichloroethane. Three-hour composite samples were being collected on CMS tubes. Under the meteorological conditions existing during that sampling period, one sample resulted in a three-hour average concentration of 24 ppbv, while the second sample, collected less than 150 yards away, resulted in a three-hour average concentration of 142 ppbv.

Quality assurance is accomplished by using NIST-traceable standards. To determine each instrument's response at the beginning of each shift, the GC's are calibrated with the appropriate gases. The ITD's are tuned using FC-43 as the reference compound. In addition, a CMS tube is loaded with the appropriate gaseous standards for analysis by each GC/ITD. One set of duplicate CMS tubes is collected each shift. This duplicate collection is rotated to a different van each

shift. Each shift, an audit CMS tube is prepared for each GC/ITD operator. Figure 1 depicts the results which can be achieved by this analytical scheme if attention is paid to detail.

The report subsequent to the sampling and analytical activity tabulates the results. The real-time and the three-hour CMS composite results are formatted in a manner such that the sampling location and meteorological data are also available to the report reviewer. The final results are reviewed by Health Effects personnel to determine if any of the reported concentrations could be detrimental to the general public. If substantial exceedances of the health effects levels are observed, the appropriate compliance and/or enforcement action is initiated.

Acknowledgements

I want to take this opportunity to acknowledge the cooperation and support of the following TACB groups:

- Logistics Section, Ambient Monitoring Division
- Sampling and Analysis Division
- Health Effects Division
- Technical Services Division
- Compliance and Enforcement Divisions
- Regional investigators and staff

**AUDITS OF
COMPOSITE SAMPLES
(ppbv)**

Sample Identification	Benzene	
	True	Found
Audit 2	10	14
Audit 3	10	10
Audit 4	10	14
Audit 5	10	14
Audit 6	10	10
Audit 7	10	11
Audit 8	10	12

**DUPLICATES OF
COMPOSITE SAMPLES
(ppbv)**

Sample Identification	Benzene	Styrene
305-1A	5	trace
305-1AD	5	trace
650-2A	1	10
650-2AD	1	10
940-3A	5	90
940-3AD	6	100
305-4A	22	20
305-4AD	23	20
650-5B	3	50
650-5BD	4	50
305-7A	80	380
305-7AD	130	400
650-8A	10	170
650-8AD	10	160

Figure 1. Results of Audit and Duplicate Samples

THE ESTABLISHMENT AND OPERATION OF AN NMOC
AND ALDEHYDE MONITORING PROGRAM --
EXPERIENCE OF A STATE AGENCY

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ABSTRACT

To meet the requirements of U.S. EPA's Post-1987 ozone SIP strategy for southeastern Wisconsin, WDNR undertook an NMOC and aldehyde monitoring program. Rather than invest in participation in the U.S. EPA national NMOC monitoring program, Wisconsin applied the funding to purchase of the equipment necessary to conduct the sampling and analysis on its own. In addition to the required NMOC monitoring, WDNR had a need for speciation as well as to conduct aerial sampling. A description of the equipment and procedures as well as the problems encountered and the solutions found over a three year period are presented. The quality assurance program which was devised is also presented. Special studies undertaken to deal with issues being addressed nationally are reported, i.e., pressurized vs. non-pressurized canisters, 7-day vs. weekday sampling, and interferences in the methods. Results are presented on hydrocarbon speciation, their application to chemical kinetic mechanism parameters for photochemical grid models as well as the use of aldehyde monitoring data for such mechanism parameters. Data summaries are presented for NMOCs and compared with the national program, along with aldehyde and hydrocarbon speciation summaries. Finally, the results of the quality assurance measures, i.e., data completeness, internal audits, and interlaboratory comparisons are also presented. Based on Wisconsin's experience, it should be possible for other state or local agencies to conduct their own NMOC and aldehyde sampling and analysis programs.

INTRODUCTION

Beginning in 1984, U.S. EPA began a program to measure concentrations of nonmethane organic compounds (NMOCs) in 39 urban areas in the United States (1). In September 1986, U.S. EPA announced an expanded effort to obtain NMOC concentrations in many more urban areas in the United States "in support of the ozone control program" (2). The U.S. EPA would supply the necessary sampling equipment, to be collected in passivated stainless steel canisters, and perform the analysis in its laboratories at Research Triangle Park, NC, at a cost of \$19,000 per site. A minimum of two sites, one in the core, the other at the fringe of the central business district (CDB) of each urban area were recommended to measure ozone and the precursors, nitrogen oxides and NMOC.

Rather than participate in the EPA program, Wisconsin decided to perform its own NMOC analysis. There were three reasons for Wisconsin's decision: the cost for EPA's program; the need for additional NMOC data not provided by U.S. EPA's program; and the need for speciation of the NMOC samples.

We believed the incoming, upwind precursors (as well as transported ozone) to the Milwaukee urbanized area to be higher than the EKMA model assumed in its default values. This is due to upwind large urban sources to the south and southeast of the Kenosha to Milwaukee corridor. Therefore we decided we needed to obtain incoming precursor and ozone concentrations from the south and southeast, over Lake Michigan. This was accomplished through an aerial study performed in 1987. We will not discuss that study in this paper but two reports on this study are available upon request from the authors, one a detailed report on the equipment, procedures, and data obtained (3) and the other an analysis of the data (4).

Interest in speciation resulted from our desire to develop canister techniques for air toxics and to provide the best inputs to the OZIP/EKMA modeling effort which was required by the post-1987 ozone SIP strategy of U.S. EPA. We wanted to confirm that the Milwaukee species distribution and levels were at least similar to the default levels suggested for the EKMA modeling.

EXPERIMENTAL

Year 1 - 1987

Equipment. The equipment used was based on U.S. EPA guidance provided in Method TO12 for NMOCs by cryogenic PDFID (5), i.e., passivated stainless steel canisters (PSSCs), a sampling system, a canister cleaning system, and an NMOC lab analysis system. There were several differences which are discussed below.

Procedures. Collect ambient air samples in canisters at two urban sites in Milwaukee, 6 to 9 a.m. CDT, seven days per week. The collection sites were multiple parameter air monitoring stations equipped with ozone and NO_x analyzers. Canisters were returned to a field lab in Milwaukee daily for PDFID analysis for NMOC. Sixteen canisters were set aside for the U.S. EPA ASRL lab at Research Triangle Park, NC for gas chromatographic analysis with an FID detector for over 100 species; ten canisters were sent to the Wisconsin State Lab of Hygiene (WSLOH) for total NMOC by GC analysis (sum-of-species). Collect

a second canister sample once every 14 days at each site (once per week at alternating sites) for determination of precision of the sampling method.

Problems/Solutions. The initial PDFID system included a small GC with a small oven that could not hold the cryogenic trapping column. Instead the trapping column was placed outside the oven and heated with a hot water bath (6). Inside the GC oven a blank unpacked column (a bypass tube) connected the gas sampling valve to the flame ionization detector. The 6-port valve for switching gases was also outside the gas chromatographic oven.

The EPA samplers, used in their national NMOC study, pressurized the canisters with a Metal Bellows MB-151 pump as an air mover with an appropriate valve. We were unable to get the MagnelatchTM valves in time for the study and instead used air operated bellows valves (NuproTM SS-4BK-1C). We found that these valves worked well and that a small cylinder (80 cu ft) of compressed nitrogen was sufficient for our summer field study. Unlike the Magnelatch, no special circuit is required to prevent the valve from heating up. To reduce site visits we built samplers able to handle 3 canisters at one time (for weekends).

The 1987 canister cleaning system followed the design in the U.S. EPA Method T012. While the canister system worked, the clean air system was not consistent in clean air production. The clean air system had no holding reservoir to store clean air and the direct air flow from the system was very slow. Canisters were humidified by direct injection of HPLC-grade water. After the first year we evaluated the system and made some significant changes for the 1988 study.

Year 2 - 1988

Equipment and Procedures. The sampling and analysis set-up was similar to 1987 with the following exceptions:

- 1) A heated valve compartment was added to the 6-port chromatographic valve to prevent cold spots; this improved the precision of the method.
- 2) Cleaning system changes were made, as follows: a) replaced the zero air source with a commercial tank of zero monitoring air, (a final liquid argon trap was retained); the tank supplied air of more consistent quality and allowed faster fill rates which improved the cleaning system, doubling throughput from 6 canisters per day to 12 (a 150 cubic foot cylinder of zero monitoring air supplied enough gas to clean over 80 canisters); b) humidification by direct injection of HPLC grade water was replaced with humidification of the zero air by passing it through a high pressure water bubbler (as now recommended in T0-12); this bubbler was constructed from a two-valve sampling canister; c) we replaced the critical orifice for zero gas control with a mass flow controller to better regulate the gas flow and decrease the canister fill time.
- 3) Aldehyde sampling was initiated. A sampler consisting of an oilless pump (Thomas - low volume, low pressure), a timer with an elapsed time meter, a mass flow controller (~1 ppm), two electrically operated solenoid valves, with appropriate tubing connected to the glass sampling manifold used for NMOC analysis. A cartridge, prepared by the WSLOH by coating purified DNPH on a Waters Associates "SepPAK" silica gel

cartridge, was inserted for each sample. The timer was set to operate between 6 to 9 a.m. each day, collecting 180 liters of air. The cartridges were removed and sent to the Occupational Health Lab of the WSLOH for analysis utilizing U.S. EPA Method T011 (7).

Year 3 - 1989

In 1989 the only change made was that we brought on-line a standard laboratory GC (Hewlett Packard HP5890) in the PDFID analysis system in place of the HNU small GC, placing the cryogenic trapping loop inside the GC oven. This brought improved performance. Analysis time was reduced from 9 minutes to 5 minutes. The minimum detection limit was reduced from 50 to 20ppbC. Precision was improved for propane working standards. In 1989, 79% of all samples were analyzed in a minimum of two runs with an average deviation of 5.9% for all samples. The correlation of the new PDFID analysis system with the gas chromatographic analysis performed by the WSLOH improved from 0.904 to 0.998. However, a 7-10% negative bias was noted for the new system compared with the old.

Quality Assurance

As with much of the NMOC program at the time, there was little available information about setting up a quality assurance program for this study. Drawing on our experience with other monitoring projects, we set up a program of our own. This included the writing of an EPA-approved quality assurance project plan as well as standard operating procedures for sampling and analysis. Specifics of the QA program included:

Field. 1) Co-located canisters for precision (duplicate samples); 2) pre- and post-season sampler audits; 3) co-location of sampling systems following the sampling season.

Lab. 1) Daily calibration with working propane standards (900 ppbC) certified against a National Institute for Standard SRM; 2) use of both propane and ambient-air control gases; 3) analysis of selected samples for total NMOC by gas chromatography conducted at the State Laboratory of Hygiene (sum-of-species method); and 4) interlaboratory exchange of samples with U.S. EPA laboratories (EMSL and ASRL).

RESULTS AND DISCUSSION

Pressurized vs. Non-Pressurized Canisters

The Wisconsin program used the MB-151 pump to fill canisters to 30 psia or greater as described in U.S. EPA Method T012. We analyzed selected pressurized canisters, vented the canisters to atmospheric pressure and reanalyzed the canisters. The results showed a positive bias, with the NMOC concentration consistently higher (average 12.3%; range <1% to 25%) for the non-pressurized canister. The result of this study does not show that pressurized canisters are more accurate than non-pressurized but does show that results from the two methods can not be compared without some consideration of the bias.

7-Day vs. 5-Day Sampling

Wisconsin decided to collect 6-9 a.m. samples every day of the week while the U.S. EPA program has remained a 5 weekday program. A

comparison of the NMOC results for weekday vs. the weekend samples was made. The distribution of NMOC data shows that the weekend NMOC data are not significantly different than the weekday data. The 7-day means vs. the 5-day means were 0.324/0.338 for the Civic Center Site and 0.454/0.510 for the North site. U.S. EPA's choice of weekday sampling was based on the theory that the heaviest vehicular traffic occurs in the early morning on working days in the central business district of urban areas. While it is true that for many urban areas there is little vehicular traffic in the central business district on weekends, that is not necessarily the case for Milwaukee. On weekends leisure time activities at the lake shore (which is adjacent to the central business district) attracts very large numbers of people (with their vehicles). This is confirmed by the results of our weekday vs. weekend comparison.

Other Studies (of Potential Interferences)

Fluorocarbon dusting spray. In 1988 an intermittent contamination problem developed with one brand of canisters. The problem was eventually traced to a fluorocarbon dusting spray used on the canister valves prior to analysis. The fluorocarbons became trapped in a small dead space on the valve and would leak out during analysis. We discontinued use of any dusting spray and valves are now cleared by a momentary venting of canister contents.

Aldehyde/Ozone Interactions. Recently Arnts and Tejada (8) reported ozone interference in the DNPH cartridge method for aldehydes. He reported that placement of a potassium iodide coated copper tubing inlet in front of the cartridge appears to eliminate the interference. We are currently experimenting with that procedure in advance of our 1990 program.

Hydrocarbon Species

As stated in the introduction, we were interested in determining the hydrocarbon species present in our NMOC canister samples. Time and cost consideration made it economically unfeasible to quantitatively analyze for all compounds in all air samples. During the first year we worked to develop a list of 37 surrogate compounds to be identified and quantified in selected air samples based on data from a number of literature sources. Using data from the 1987 and 1988 field studies, the list of surrogate compounds was expanded to 50 compounds for 1989. The new surrogate list resulted in a reduction of the unidentified compounds from an average of 32.5% (3.2 to 79.5%) to an average of 19.6% (6.5 to 33.9%). Gas chromatographic analysis of air samples yielded concentrations that would be condensed in seven modeling parameters used for the CB-IV mechanism (9).

A comparison of the computed modeling parameters determined using the 37 surrogate compounds versus an extensive GC analysis provided by U.S. EPA (for over 100 species) (10) did show a difference in the modeling parameters calculated. For twelve samples, four of the modelling parameters - PAR, TOL, XYL, ALD2 - had percent differences greater than -25% and one modeling parameter - OLE - had a percent difference greater than -50%.

Aldehydes

While the CB-IV mechanism provides for the calculation of a surrogate aldehyde fraction from the hydrocarbon profile data the accuracy of that fraction is questionable. When modeling parameters were calculated from the sampling data the FORM and ALD2 fraction were found to be much less than the default values in the EKMA model. The U.S. EPA default value for FORM is 0.021 and for ALD2 it is 0.052. Reduction of our data yielded FORM fractions of 0.000 in 1987 and 0.002 in 1988 and ALD2 fractions of 0.008 in 1987 and 0.010 in 1988. We attempted to compare fractions from the aldehyde analysis utilizing Method T011 with that calculated from the NMOC species. The comparison based on limited amount of data indicates the actual aldehydes were greater by two to eight times the computed values, closer to the default values. This comparison has raised concern and convinced us that the estimation of the aldehyde modeling parameters from NMOCs is inaccurate and that aldehyde sampling and analysis is required for accurate CB-IV computations.

Data Summary

NMOC Summary. A summary of Wisconsin NMOC data results is available upon request. As with the data reported by U.S. EPA (11) the NMOC concentrations are lognormally distributed. The geometric mean suggests that NMOC decreased at both sites from 1987 to 1988. A decrease is seen at the Civic Center site in 1989 but the North site changed little.

NMOC Comparison. In 1987 the Wisconsin site mean was less than that reported for the U.S. EPA national study (12). Comparing the summary data, the UWCC site was 24/34 ranked by mean (21/34 by median) and the UWN site was 26/34 by mean (29/34 by median). In 1988 the Wisconsin sites mean (0.365 ppmC) was much less than that reported by U.S. EPA (0.636 ppmC). The UWCC site would rank 33/40 (34/40 median) sites and the UWN site would rank 37/40 (36/40 by median) sites by mean.

Aldehyde results. We collected three-hour aldehyde samples on forecast high ozone days. In 1988 for 37 samples, the mean formaldehyde was 6.3 ppb and the mean acetaldehyde was 4.2 ppb; in 1989 for 26 samples, the mean formaldehyde was 3.7 ppb and the mean acetaldehyde was 2.2 ppb. A complete data summary is available upon request.

Speciation Results. A complete list of data from the GC analysis is available upon request. To summarize the 1988 data, the WSLOH analyzed 37 canisters for 39 surrogate compounds and the U.S. EPA - ASRL analyzed 11 of the 37 canister samples for over 100 compounds. Of the 50 most common compounds found by ASRL, 29 were paraffins, 7 were olefins, and 14 were aromatic. The WSLOH found isobutane was the most common paraffin with a mean concentration of 33 ppbC. Acetylene and ethylene were the most common olefins and together with ethane had a mean concentration of 26 ppbC. Toluene was the most common aromatic with a mean concentration of 25 ppbC. ASRL found similar concentrations.

Quality Assurance

Data Completeness. The Wisconsin NMOC monitoring plan called for seven day sampling during the period from Memorial Day until Labor Day. Data completeness for 1987 was 92%, for 1988 was 96%, and for 1989 was

92%. All invalid samples were the results of sampling problems, such as incorrectly set timer or canisters improperly attached to the sampler. This compares with the U.S. EPA reported a completeness of 95.0% in 1987 and 93.4% in 1988 for the national study (11,12).

Internal Audits. Both pre-season and post-season audits were performed in 1988 and 1989. These audits were devised in consultation with our Quality Assurance Coordinator. Clean canisters were connected to the samplers at the sampling site. Using a modified CSI 1700 gas phase titration unit, audit gases were prepared and connected to the sampler for a short sampling period. The canisters were removed and returned to the laboratory for analysis and the results were compared to the expected concentrations. Four NMOC concentrations, including a blank, were collected at each sampler. Audit goals of $\pm 25\%$ for accuracy were met for most of the audits samples. There were some failures, believed to be due to auditing errors more than to system failures. Problems include incorrectly blending gases and carryover of higher concentration NMOCs.

Interlaboratory comparison. We exchanged NMOC samples with two U.S. EPA laboratories located at Research Triangle Park, the EMSL-QA lab and the ASRL lab. The EMSL lab testing was a direct comparison of PDFID methods and agreement was quite good: correlation coefficients varied from 0.936 to 0.998 over three years. The ASRL comparisons, with sum-of-species, were less favorable. Lonneman (22) reported a "moderately high positive bias" for the PDFID compared with his GC sum-of-species method. He attributed this to oxygenated hydrocarbon species, which showed up on the chromatogram as broad tailing peaks. Those broad peaks are not integrated by the GC method but are incorporated in the NMOC peak detected by the PDFID method. By converting from the hot water bath to the GC oven for the PDFID method, we found better agreement with the WSLOH sum-of-species data for 1989, believed to be due to better resolution of the oxygenated species in the PDFID peak integration. We have not as yet received the 1989 speciation data from the ASRL lab at U.S. EPA.

CONCLUSION

Based on Wisconsin's experience, it should be possible for other state or local agencies (or private consultants) to successfully establish, operate and maintain NMOC and aldehyde sampling and analysis programs. Techniques of quality assurance should be adapted such as: round-robin testing; blind audit samples; precision (replicate sampling) and accuracy (analysis of standards); and external audits. Aldehyde sampling and analysis is also feasible so long as the ozone interference as reported by Arnts-Tejada (8) is removed (utilization of a potassium coated copper tubing ozone cutter). Speciation of hydrocarbon species is also possible but more difficult and expensive. A major pitfall in the NMOC analysis is possible interference by oxygenated species. The selection of appropriate surrogate species is also a consideration.

We recommend that U.S. EPA, through the Quality Assurance Office, formalize the interlaboratory testing program for NMOC analysis by PDFID, as well as for aldehydes, as more states develop their own programs. In addition, goals for precision and accuracy should be developed by U.S. EPA and audit gases made available for state use.

ACKNOWLEDGEMENTS

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**DISCREPANCIES IN AMBIENT NON-METHANE HYDROCARBON
MEASUREMENTS AMONG VARIOUS METHODS**

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Previous studies have acknowledged a discrepancy in measurement of ambient Non-Methane Hydrocarbons (NMHC) between continuous analyzers and manual methods such as the Pre-Concentration Direct Flame Ionization Detection (PDFID) and "sum of species" obtained by gas chromatography.

The Ventura County Air Pollution Control District has been making comparison measurements between Combustion Engineering 8202A continuous NMHC analyzers and the PDFID technique since 1987, and additional comparison with C2-C10 speciation during 1989. Additionally, the EPA's "Non-Methane Organic Compound" Program made PDFID measurements at twelve locations in California where Combustion Engineering 8202A analyzers were making simultaneous measurements. These data as well as the data from other tests are presented and used to identify some of the factors that influence this difference in measured NMHC.

These studies have significant implications in determining a representative method for ambient hydrocarbon measurement.

Introduction

For some time persons involved with ambient hydrocarbon measurement have recognized discrepancies between various non-methane hydrocarbon monitoring methods. Data from continuous non-methane hydrocarbon (NMHC) analyzers have not only been shown to compare poorly with manual methods such as the Pre-Concentration Direct Flame Ionization Detection (PDFID) method. Also, two identical continuous analyzers produce quite different data when sampling side by side.

Results of comparisons between Combustion Engineering 8202A continuous analyzers and three hour integrated samples analyzed by the PDFID method were presented at the 1988 International Symposium on Measurement of Toxic and Related Pollutants. That study demonstrated the poor agreement between the two methods, analysis of the data showed large sample to sample variation between the methods as well as a distinct difference between the two sites studied.

These studies initiated by the Ventura County Air Pollution Control District in 1987 was continued during 1988 and 1989, providing many more comparisons. Additional data was obtained allowing comparisons between PDFID measurements made by EPA's Non-Methane Organic Compound Monitoring Program and data generated by the California Air Resources Board and various California local air pollution districts using the Combustion Engineering 8202A. An intensive comparative study, called "the El Rio Shootout", was performed by Ventura County in 1989 to try to answer some of the questions concerning the observed site to site differences as well as the sample to sample variations at one site. This paper reports the findings of these studies.

Experimental Methods

Ventura County A.P.C.D. Comparisons

The PDFID sampling and analytical procedures and equipment as well as the operation of the Combustion Engineering 8202A's followed the procedures outlined in Reference 1. In 1989 the PDFID analytical system was modified by the addition of a Nutec automated cryogenic trap and other controlling hardware to allow for unattended automated analysis. Following this modification, inter-lab comparisons were performed with E.P.A.'s Quality Assurance Division as well as California Air Resources Board and Bay Area Air Quality Management District labs in order to confirm the continued accuracy of the Ventura County automated analytical system. Comparative measurements were made at Ventura County APCD's El Rio and Simi Valley monitoring sites.

EPA PDFID/CARB 8202A Comparisons

The procedures used in EPA's Non-Methane Organic Compound monitoring program for PDFID measurements are outlined in Reference 2. The 8202A measurements obtained from the California Air Resources Board (CARB) data bank were made by both CARB operated and local district operated 8202A's. The procedures used in operation these 8202A's follow either the CARB Quality Assurance Manual or the respective local district Quality Assurance Manual. It was assumed that these procedures were all based on the CARB operating procedures and similar.

The El Rio Shootout

During the winter of 1989 an intensive comparative study was performed at Ventura County APCD's El Rio Monitoring site. In this study, the 8202A used at the Simi Valley site for comparisons since 1988 was brought to the El Rio site and co-located with the existing El Rio 8202A which had been in place at El Rio since 1987. Three hour integrated samples were collected and analyzed by both PDFID and C2-C12 speciation by capillary Gas Chromatography for comparison to the two 8202A data sets. The speciation analysis followed the procedure outlined in reference 3. During part of the study collocated integrated samples were collected and analyzed by PDFID to allow for estimation of PDFID sampling precision.

Results

Ventura County APCD Comparisons

The El Rio and Simi Valley comparisons made in 1988 and 1989 are presented in Figures 1 and 2 respectively. These comparisons show the same pattern as was seen in the aforementioned 1987 comparisons at these sites. At El Rio it was observed that at on September 10, 1988, when the full scale range of the 8202A was changed from 0-20 ppm to 0-10 ppm the sample to sample variability between the two methods decreased dramatically as can be seen in Figure 3.

EPA PDFID/CARB 8202A Comparisons

Comparisons made in 1987 and 1988 are presented in Figures 4 and 5. Comparisons made at many sites (each with different 8202A's) reveal a significant site to site bias between the two methods and raises a question as to whether the source of the bias is due to the site environment or to inherent differences between 8202A's.

El Rio Shootout

Figure 6 presents data from the two 8202A's as compared to the parallel PDFID measurement. Note that data from the 8202A which was relocated from the Simi Valley site compares to the parallel PDFID measurement at El Rio just as it had when this same instrument was at the Simi Site.

In order to see if the hydrocarbon mix was a influencing factor in differences between the two methods, the results of the speciated analyses were used to determine the percent light, medium and heavy hydrocarbon species in each speciated sample. Light hydrocarbons were defined as all species lighter than benzene. Medium was defined as all lighter than toluene but heavier than benzene. Heavy was defined as all species heavier than toluene. These subdivisions were used because some people theorize that the 8202A's would have the most difficult time detecting the heavier species. Therefore samples with higher percentages of heavy hydrocarbons would be the samples most underestimated by the 8202A's. Figure 7 and 8 present comparisons of the percent heavy and light species to the PDFID/8202A (PDFID measured value/8202A measured value) ratio of the sample. If there was any correlation between samples with a high percentage heavy species being most underestimated by the 8202A, then the samples with high percentage heavy species would have the highest PDFID/8202A ratio. This analysis

showed no such correlation with the heavy species or the light species.

The precision of both methods was estimated by comparison of the co-located or repeat analysis data. The 8202A precision was estimated by comparison of the co-located 8202A data during the entire study. PDFID analytical precision was determined by comparison of repeat PDFID analysis during the entire study. Total PDFID precision (analytical and sampling) was estimated by comparison of a limited number of co-located PDFID samples. A summary of the precision estimates is presented in Figure 9.

Conclusion

The "site specific" difference in comparisons between the Combustion Engineering 8202A and the PDFID measurement method appear to actually be "analyzer specific". Data from this study suggests that these observed differences are related to some factor(s) inherent to each individual analyzer. Furthermore, results of this study indicate that there is no correlation between changes in the ambient hydrocarbon mix and observed differences between the two monitoring methods.

Using the lowest possible full scale range when operating a Combustion Engineering 8202A is extremely important. Data from this study suggests that operating on ranges greater than 0-10 ppm full scale results in extremely poor precision. Even when the 8202A is operated on 0-10 ppm full scale, the precision of the 8202A is much less than that of the PDFID method.

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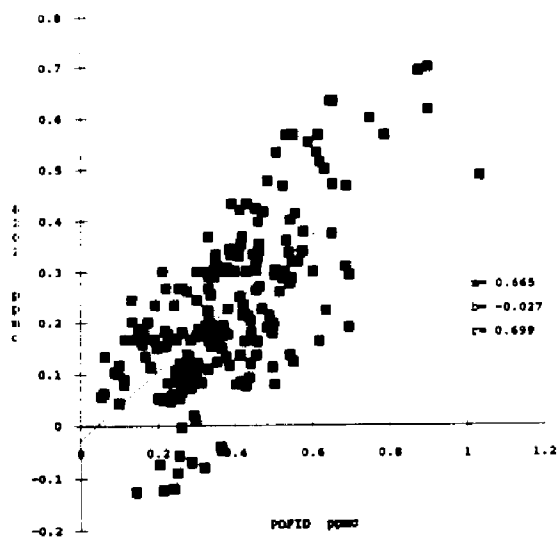


Figure 1. El Rio 1988 & 1989: PDFID vs. 8202

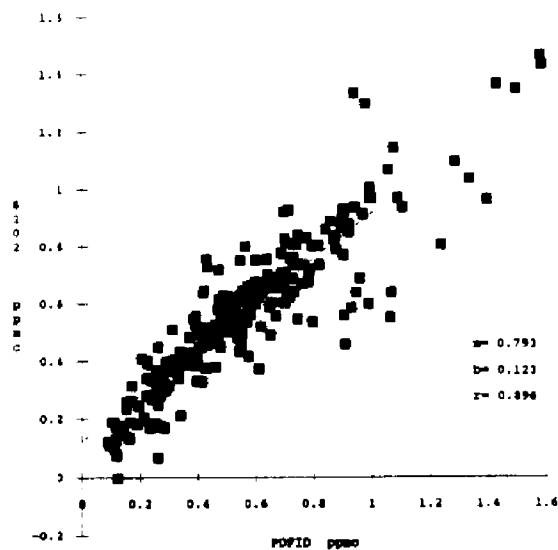


Figure 2. Simi Valley 1988 & 1989: PDFID vs. 8202

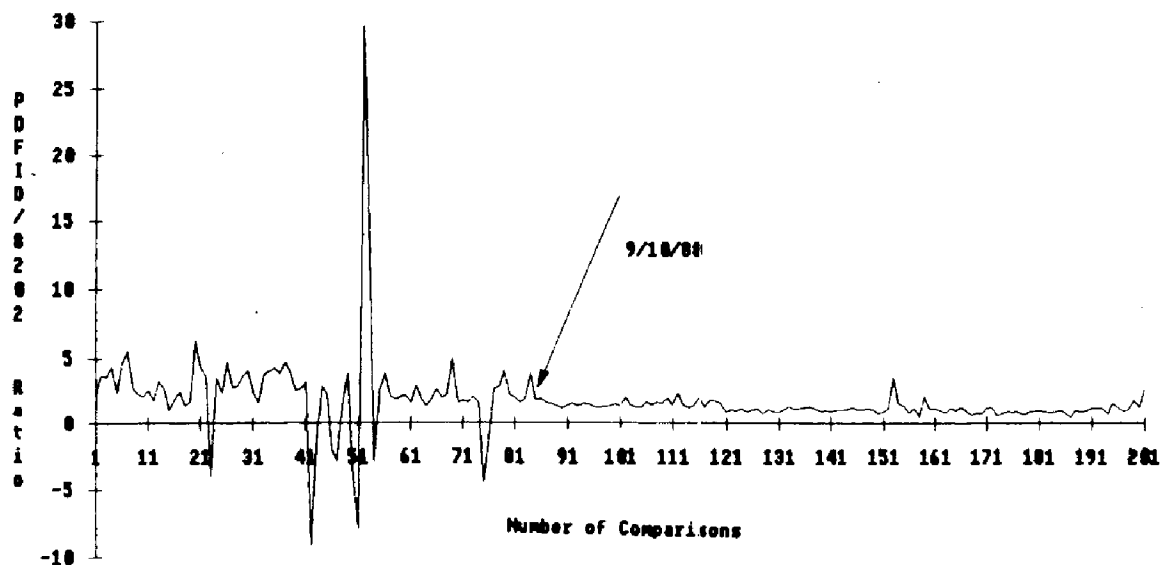


Figure 3. El Rio 1988 & 1989: PDFID/8202 Ratio

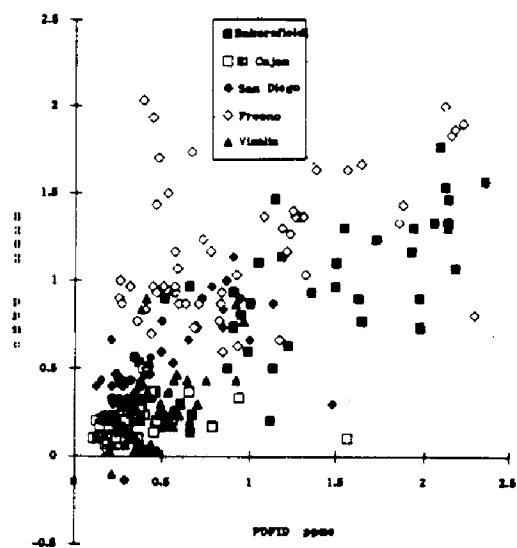


Figure 4. 1987 PDFID vs. 8202: 5 Locations

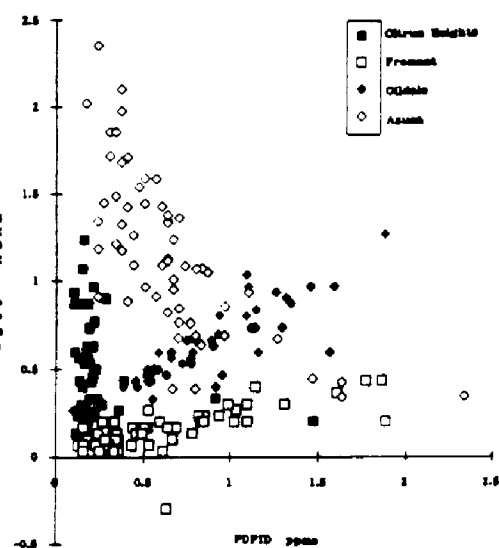


Figure 5. 1988 PDFID vs. 8202: 4 Locations

**Figure 6. El Rio Shootout:
8202/8202/PDFID**

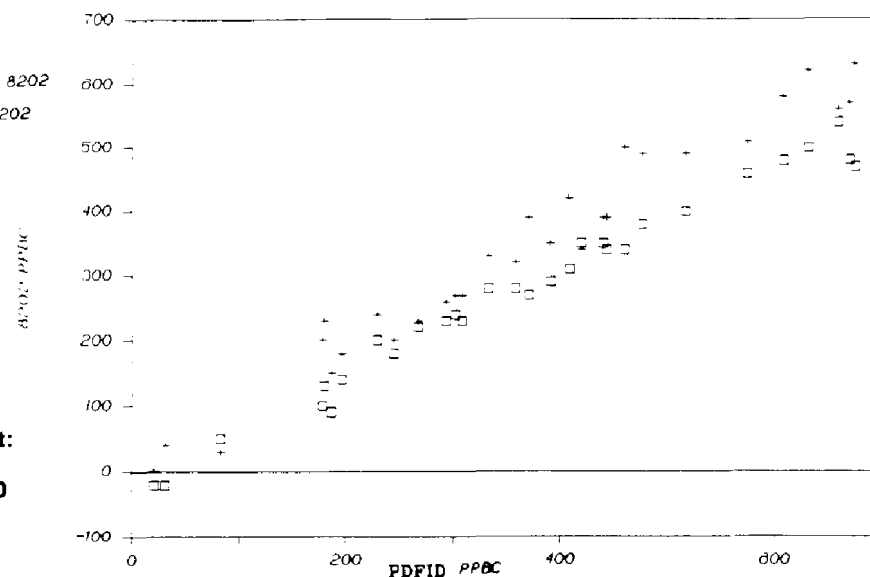


Figure 7. % Heavy vs. PDFID/8202 Slope

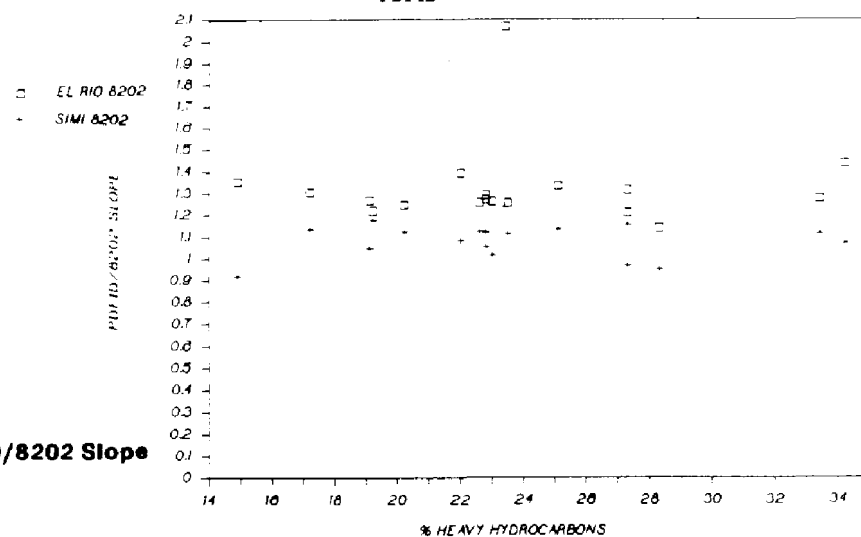
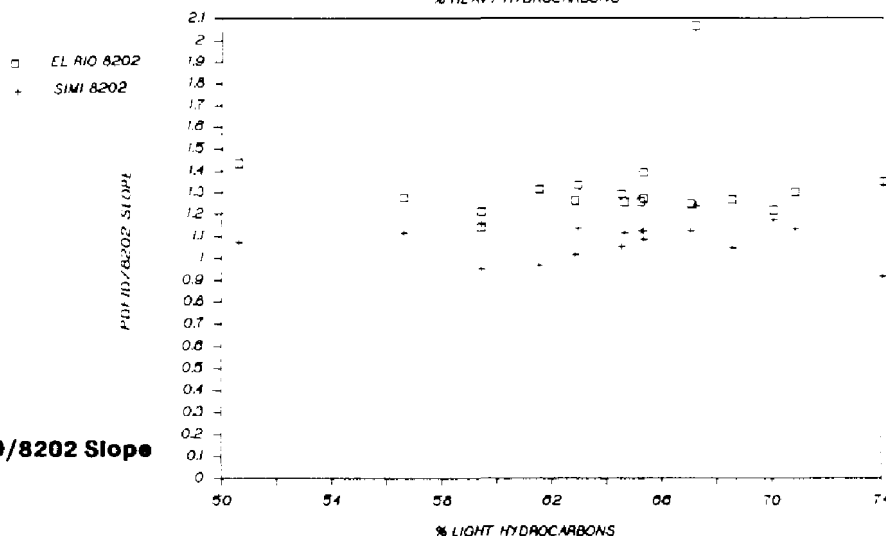


Figure 8. % Light vs. PDFID/8202 Slope



	Overall Precision - 8202	Overall Precision - PDFID	Analytical Precision - PDFID
Absolute Difference Mean	61.667	9.250	7.500
Standard Deviation	46.169	6.886	7.583
Percent Difference Mean	19.895	7.017	2.161
Standard Deviation	16.298	4.514	2.892

Figure 9. El Rio Shootout Precision Summary: 8202 and PDFID Methods

MEASUREMENT OF ACID DEPOSITION COMPONENTS
IN SOUTHERN COMMERCIAL FORESTS

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The role of acid deposition within rural areas of the southeastern United States in general, and commercial pine forests in particular, may be involved in the observed decline of forest productivity in the region. The University of Florida has established monitoring sites at three rural locations -- Duke Forest (near Durham, NC), Austin Cary Forest (near Gainesville, FL), and Stephen F. Austin Forest (near Nacogdoches, TX). This study, which is funded by the U.S. EPA, entails monitoring within a cleared area in conjunction with controlled artificial exposure studies of pine seedlings by forestry researchers. Of particular interest are the relative amounts of wet deposition components at these sites. Collection of wet deposition samples is performed by an automated wet-dry bucket collector. Samples are shipped to the Air Pollution program laboratories, Environmental Engineering Sciences Department, University of Florida, for detailed analysis by ion chromatography and atomic absorption spectrophotometry. Comparisons between sites over the period of operation (minimum of 18 months for each site) will be made, as well as observation of seasonal and annual variations at the sites. In addition, comparisons will be made between the Florida cleared site and an adjacent site within the forest canopy.

INTRODUCTION

Awareness of the apparent effects of acidic deposition (primarily in the form of H_2SO_4 and HNO_3) upon the forests of eastern North America has existed for the past two decades.^{1,2} However, the focus of attention has been limited primarily to the northeastern United States and eastern Canada. No comprehensive study to date has addressed the possible effects of acidic deposition upon commercial forests in the southeastern United States. The Southern Commercial Forests Research Cooperative (SCFRC) was established as part of the Forest Response Program (FRP), National Acid Precipitation Assessment Program (NAPAP), to thoroughly study commercial pine forests in regard to the possible effects of acidic deposition on various species of southern pines.

EXPERIMENTAL

Site Selection

The location of three monitoring sites established by the University of Florida as part of the Atmospheric Exposure Cooperative (AEC) supporting the SCFRC program is shown in Figure 1. All sites are situated in cleared

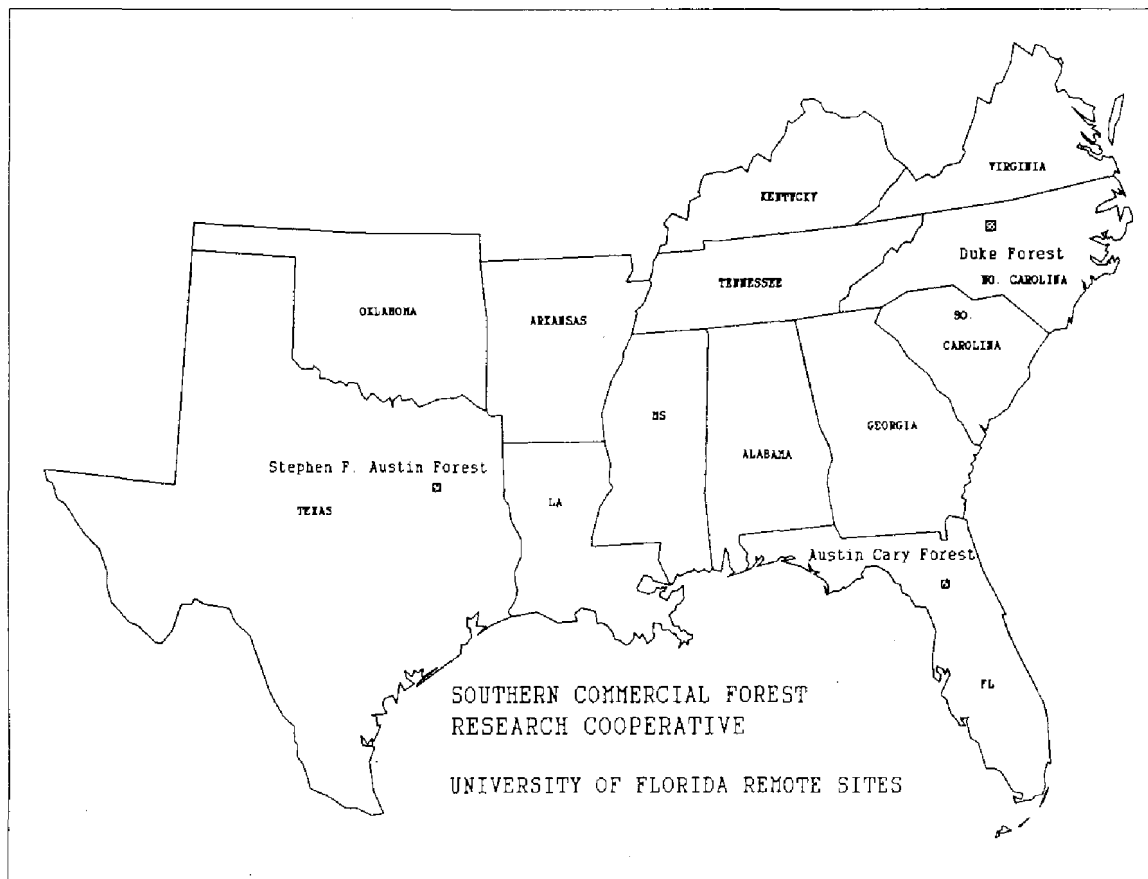


Figure 1. SCFRC Monitoring Sites

areas within commercial loblolly, slash, and short leaf pine plantations located at Duke Forest, in north central North Carolina; Austin Cary Forest, in north central Florida and Stephen F. Austin Forest, in east central Texas, respectively (hereafter referred to as NC, FL, and TX). The periods of sampling for the data reported in this paper was from January

1988 to December 1989 for the NC site and from July 1988 to December 1989 for the FL and TX sites. In addition, sampling has been carried out at a site in the Integrated Forest Study network (hereafter referred to as IFS). The latter site is located approximately 2 km northeast of the FL site but within the forest canopy. The period of sampling at the IFS site was from May 1988 to May 1989.

Field Sampling

Wet deposition samples are collected at all sites using Aerochem Metrics Model 301 Automated Wet-Dry Deposition Collectors (Bushnell, FL). Samples are analyzed at each site for pH and conductivity using a Markson Model 4603 Solution Analyzer (San Diego, CA). A 250 mL aliquot of each event (whenever possible) is shipped to the Air Pollution Analysis Laboratory in a cleaned HDPE bottle under refrigeration. Precipitation amounts are measured by a Climatronics tipping bucket rain gauge (Bohemia, NY) and recorded by an Odessa Model DSM-3260 Datalogger (Austin, TX). At the IFS site, precipitation sample volumes of 500 mL are collected from automated wet-dry deposition collectors, from stemflow collectors and from open containers on the forest floor (throughfall).

Laboratory Analysis

Upon receipt of wet deposition samples, aliquots are taken for measurement of pH and conductivity. The remainder of the sample is filtered through a 0.45 micron Nalgene filter assembly and the filtrate stored in a separate, labelled 125 mL HDPE bottle and refrigerated at 4 degrees C for later analysis. The general methods and protocols for the detailed analysis of precipitation have been previously reported.³ Conductivity and pH measurements are performed with a Markson Model 4603 Solution Analyzer, flame atomic absorption measurements are performed with a Perkin-Elmer Model 5100 Atomic Absorption Spectrophotometer (Norwalk, CT) and ion chromatograph measurements are performed with a Dionex Model 4000i Ion Chromatograph with separate columns for separation and analysis of inorganic anions and monovalent cations (Sunnyvale, CA).

RESULTS AND DISCUSSION

Annual precipitation amounts observed at the SCFRC sites for the years 1988 and 1989 are shown in Table 1. At the NC site, there was a 57 percent increase in precipitation from calendar years 1988 to 1989. Because the FL and TX sites began operation at the start of the third quarter of 1988, comparison of annual precipitation amounts cannot be made. However, the amounts of precipitation at the FL and TX sites during the last half of 1989 are lower than for the last half of 1988 by 29 percent and 23 percent, respectively.

Table 1. Precipitation Amounts at SCFRC Monitoring Sites

Site	Amount in 1988 (cm)	Amount in 1989 (cm)
NC	99.52	155.98
FL	88.27*	109.25
TX	42.65*	128.22

* - Last two quarters of 1988 only

pH and Conductivity

Volume weighted averages for hydronium ion concentration and conductivity at the SCFRC sites (shown as annual averages) are presented in Figure 2. It is apparent that the NC site has the most acidic precipitation of the three monitoring sites in the network. The FL and TX sites show nearly equivalent values for hydronium ion concentration and conductivity on an annual basis. Typical weather patterns show an uptake in moisture from the Gulf of Mexico at these sites, while the NC site weather patterns indicate the possibility of long-range transport of acidic deposition precursors from inland areas.

Comparison of pH values recorded at the sites and later at the Air Pollution Analysis Laboratory show a general increase in pH values (usually less than 0.1 pH units) during sample transit. It has been reported that an apparent increase in pH is likely due to microbes decomposing acetic and formic acids initially present in the sample.^{4,5}

Major Inorganic Anions

The project protocols require that only the major inorganic anions (Cl , NO_3 , total SO_4 and HPO_4) are to be analyzed. The annual volume-weighted averages for these anions at the SCFRC sites are presented in Figure 2. The levels of SO_4 and NO_3 at the NC site are higher during the period of study, reflecting the increases in hydronium ion concentration and conductivity at this site. Elevated levels of SO_4 and NO_3 are also apparent for the FL and TX sites, although the concentrations on an annual basis are nearly identical. However, the Cl levels at the FL and TX sites are noticeably higher during the period of study, whereas the NC site showed no marked annual variation. Again, the apparent weather patterns for the uptake of water vapor involving the FL and TX sites might account for this unique variation.

Major Cations

The annual volume-weighted averages for the major cations at the SCFRC sites are presented in Figure 2. At the NC site, higher concentrations of Ca and NH_4 are indicated for precipitation during 1988. All levels of cations at the NC site are higher in 1988 than in 1989 due probably to decreased precipitation amounts in 1988. At the FL and TX sites, the annual averages for the divalent cations (Ca and Mg) and K are nearly identical between years and sites. However, the annual average for Na is noticeably higher in 1988 at the TX site and in 1989 at the FL site. This may indicate the relative contribution of sea water uptake at these sites.

SCFRC - IFS INTERSITE COMPARISON

The IFS site utilizes three different types of wet deposition collectors: automated wet/dry deposition collectors in a cleared area and within the forest canopy (abbreviated as WF), stemflow collectors for measurement of deposition that runs down the exterior of the tree (abbreviated as SF) and throughfall collectors placed in specified areas on the forest floor within the canopy (abbreviated as TF).

The data for the major components measured in wet deposition at the FL and the IFS sites are presented in Table 2. Comparison of hydronium ion volume-weighted concentration values shows that collection outside of or within the forest canopy is not a crucial factor. In addition, values for

most analytes are similar for the WF data from the IFS site and the FL SCFRC site. Samples gathered by SF and TF collectors show a large increase in the concentration of most analytes, which might be caused by leaching from the exterior surfaces of the trees or by washing off of particles dry deposited the tree surfaces. The only exceptions were for NH_4 and for NO_3 , which indicate that those components are presumably utilized by the trees or other organisms during and after the precipitation event.

Table 2. Statistical Summary of FL and IFS Wet Deposition Data
(all concentrations in micromoles per liter)

Site and Collector	$\text{SO}_4=$	NO_3^-	Cl^-	$\text{HPO}_4=$	H^+	NH_4^+	K^+	Na^+	Ca^{++}	Mg^{++}
FL 1988	13.34	10.05	11.69	0.72	23.50	5.88	0.84	18.34	11.99	5.67
FL 1989	17.35	15.25	25.50	1.19	27.76	12.16	1.54	31.01	15.79	7.72
IFS WF Collectors	30.66	13.95	17.70	0.83	22.99	9.49	1.10	21.61	21.67	11.70
IFS TF Collectors	44.72	18.24	44.96	1.30	23.12	4.71	5.77	56.26	48.68	25.02
IFS SF Collectors	180.70	11.24	210.45	2.39	211.40	2.38	16.65	136.24	161.82	80.53

CONCLUSIONS

It has been found that wet and dry deposition samples collected at the NC site contained higher levels of nearly all acidic deposition precursors than the FL or TX sites while samples obtained at the FL and TX sites are remarkably similar. One disturbing trend was found in the calculation of ion balances at all sites. Typically the anion budget in wet deposition (in microequivalents per liter) is lower than the cation budget by a factor of twenty to thirty percent. The likely cause of this deficit is the failure to preserve and immediately analyze samples for the weakly ionized organic and inorganic species. Earlier research has found that organic acid components in wet deposition may contribute between 15 to 35 percent of the free acidity present.^{4,5} Currently field samples are being preserved by the addition of chloroform on site before shipment in order to analyze for these weakly acidic components.

ACKNOWLEDGEMENTS

We wish to thank our site operators in the SCFRC network (Rafael DePaz, David Anthony, David Vermillion, Asgar Mirza, Robert Yeh, P. Brian Morlock) for the collection of samples and maintenance of the sites. In addition, the efforts of our undergraduate students in the Air Pollution Analysis Laboratory (Richard Hutton, Allen Preston, Jose Garcia, Rodney Phillips, Daniel Green, Ken Kohn, Michael Pring, Mark Roberts, Kim Owen) for the prompt analysis of wet deposition samples are greatly appreciated. Finally, the cooperation of research colleagues at the IFS network site (Dr. Henry Gholz, David Nolletti and Steve Snitherman of the Department of Forestry, University of Florida) is gratefully acknowledged.

DISCLAIMER

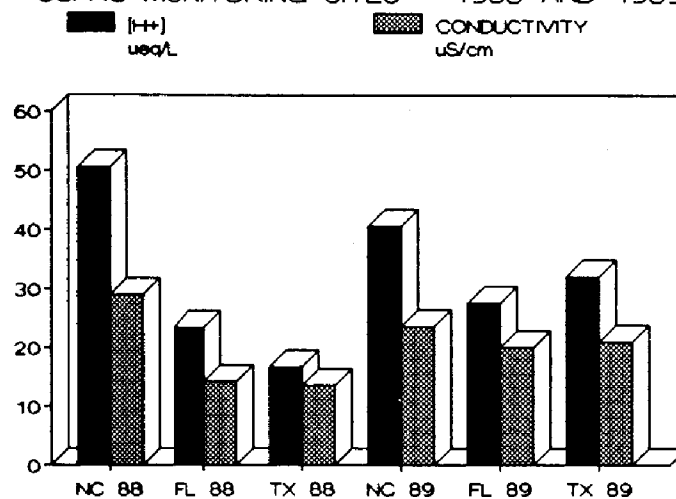
This research was supported by funds provided by the U.S. Environmental Protection Agency within the joint U.S. Environmental Protection Agency - USDA Forest Service Forest Response Program in cooperation with the National Council of the Pulp and Paper Industry for Air and Stream Improvement (NCASI). The Forest Response Program is part of the National Acid Precipitation Assessment Program. This paper has not been subject to EPA or Forest Service peer review and should not be construed to represent the policies of either agency.

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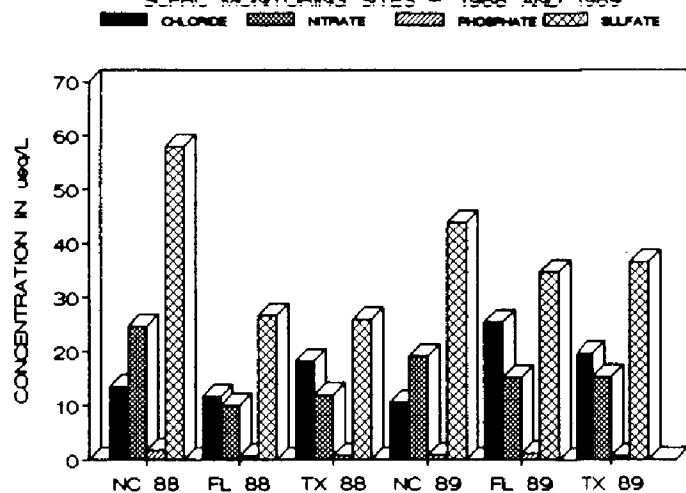
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Figure 2. SCFRC Wet Deposition Annual Volume-Weighted Averages

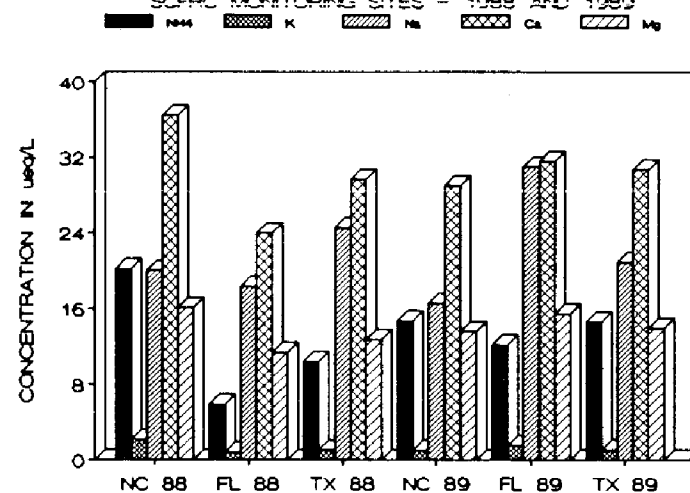
ANNUAL VOLUME WEIGHTED AVERAGES SCFRC MONITORING SITES - 1988 AND 1989



ANNUAL VOLUME WEIGHTED AVERAGES SCFRC MONITORING SITES - 1988 AND 1989



ANNUAL VOLUME WEIGHTED AVERAGES SCFRC MONITORING SITES - 1988 AND 1989



PM-10 HI-VOL COLLECTION AND QUANTI-
TATION OF SEMI-VOLATILE METHOXYLATED
PHENOLS AS TRACERS OF WOOD SMOKE
POLLUTION IN URBAN AIR

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Methoxylated phenols, including guaiacol (2-methoxyphenol) and its derivatives have been shown to have consistent concentrations in the smoke from 28 different wood stoves and fireplaces regardless of the type of wood burned or operating conditions, suggesting that they would be useful organic tracers of atmospheric wood smoke pollution. To test this hypothesis, a PM-10 Hi-Vol was modified to utilize quartz filters backed by polyurethane foam sheets (PUF) to allow quantitative collection of the methoxylated phenols while maintaining the 40 cfm air flow required for a 10-um cutoff. Twenty-four winter Hi-Vol samples were collected in Minneapolis and Salt Lake City to represent air impacted by hardwood and softwood burning, respectively, and approximately 60 semi-volatile and particulate-associated organics including phenols, methoxylated phenols, alkanes, and PAHs have been quantitated in each filter and PUF extract. GC/MS analysis of the unfractionated extracts showed that phenols and methoxyphenols accounted for the largest quantity of the semi-volatile organics collected, while n-alkanes (C₁₄ and larger) and PAHs (acenaphthylene and larger) accounted for an average total of only ca. one-third of the semivolatiles. All of the guaiacol derivatives (except formylguaiacol) had nearly identical relative concentrations in chimney smoke and in the urban air samples indicating that guaiacols have sufficiently long lifetimes to be useful as wood smoke tracers. ¹⁴C analysis was performed on each filter to determine "new" (assumed to be from wood smoke) versus "old" particulate carbon, and preliminary results show good correlation between guaiacol derivative concentrations and ¹⁴C analysis.

Introduction

Methoxyphenols, including guaiacol (2-methoxyphenol) and its derivatives, may be useful tracers of atmospheric wood smoke pollution because they are emitted at consistent concentrations from wood stoves and fireplaces regardless of the type of wood burned or operating conditions^{1,2}. As pyrolysis products of wood lignin, methoxyphenols should be unique to wood smoke in winter urban air. In an attempt to validate the use of these organics as tracers of wood smoke pollution in urban air, comparisons between the concentration of the methoxyphenols and "new" and "old" carbon (based on ¹⁴C measurements) have been conducted on 24 winter Hi-Vol samples collected in Minneapolis (primarily hardwood burning) and Salt Lake City (primarily softwood burning). The PM-10 sampler was modified to include polyurethane foam (PUF) sorbent sheets so that semi-volatile organics could be quantitatively collected under flow conditions needed to maintain the 10-um cut-off, and 60 of the most concentrated organics (including phenols, methoxylated phenols, PAHs, and n-alkanes) found in the unfractionated filter and PUF extracts were quantitated in each sample.

Experimental Methods

Three sites were chosen for each city to include residential with low vehicle traffic, residential with high vehicle traffic, and non-residential (e.g. downtown) locations. Both day and night air samples were collected at each location using a PM-10 Hi-Vol sampler that was modified to utilize quartz filters backed by two 7" X 9" X 2" polyurethane foam sheets (PUF). This modification allowed quantitative collection of the methoxyphenols and semi-volatile hydrocarbons under air flow conditions needed to maintain the 10-um cut-off. After a 12-hour sample collection (at 68 m³/hr), the filters and PUF sheets were exhaustively extracted with acetone and the unfractionated extracts were analyzed by GC/MS. Approximately 60 individual phenols, methoxyphenols, n-alkanes, and polycyclic aromatic hydrocarbons (PAHs) were quantitated in each extract based on calibration curves generated from over 50 individual standard species.

Results and Discussion

The modified PM-10 Hi-Vol sampler allowed quantitative collection (based on the absence of significant species on the back-up PUF sorbent sheet) of phenol and alkylphenols, all of the methoxyphenols (including guaiacol and syringol derivatives), acenaphthylene (M = 152) and higher molecular weight PAHs, and C14 and larger n-alkanes. As shown in Figure 1 by a GC/MS analysis of the unfractionated filter and PUF extracts from a typical Hi-Vol sample, the phenols and the majority of the guaiacol derivatives were collected on the PUF sheets, while the less volatile methoxyphenols were collected primarily on the filter. As would be expected, the largest percentage of the more volatile n-alkanes (C14 to C18) and PAHs (up to phenanthrene) also passed through the filter and were collected on the PUF.

The quantitative analyses of the unfractionated PUF and filter extracts from the urban air samples have yielded three major results:

1) Phenols and methoxyphenols are among the most concentrated semivolatile organics in winter urban air. Of the species that were quantitated in the Hi-Vol PUF and filter samples, phenols averaged 45% of the total (on a weight basis), methoxyphenols averaged 24%, n-alkanes averaged 20%, and semi-volatile PAHs (ranging from acenaphthylene to PAHs with M=252, not including alkyl-substituted PAHs) averaged 11%. As would be expected, the proportion of phenols and methoxylated phenols is higher in the residential samples (because of the higher influence of wood burning) than in the downtown samples.

2) The relative proportions of the individual guaiacol tracers found in the Hi-Vol samples is similar to those previously reported for wood smoke samples collected from chimneys², with the notable exceptions of the 4-propenylguaiacol and 4-formylguaiacol species (Figure 2). These results indicate that the majority of guaiacol derivatives emitted from wood burning have sufficiently long life-times in winter urban atmospheres to be useful tracers.

3) Although not all of the ¹⁴C results were available at the time of this report and only preliminary data analysis has been possible, the concentrations of guaiacol derivatives show good correlations with the percentage of "new" particulate carbon (assumed to be from wood smoke) determined by ¹⁴C analysis, indicating that the measurement of guaiacol derivatives could provide a reliable method for determining the relative contribution of residential wood burning to the inhalable particulate concentrations in urban air (Figure 3).

Future work will focus on determining the best individual guaiacol tracers, and will investigate the relationship between n-alkane concentrations (assumed to be primarily from vehicle exhaust in winter air) and "old" (petroleum derived) particulate carbon.

Acknowledgements

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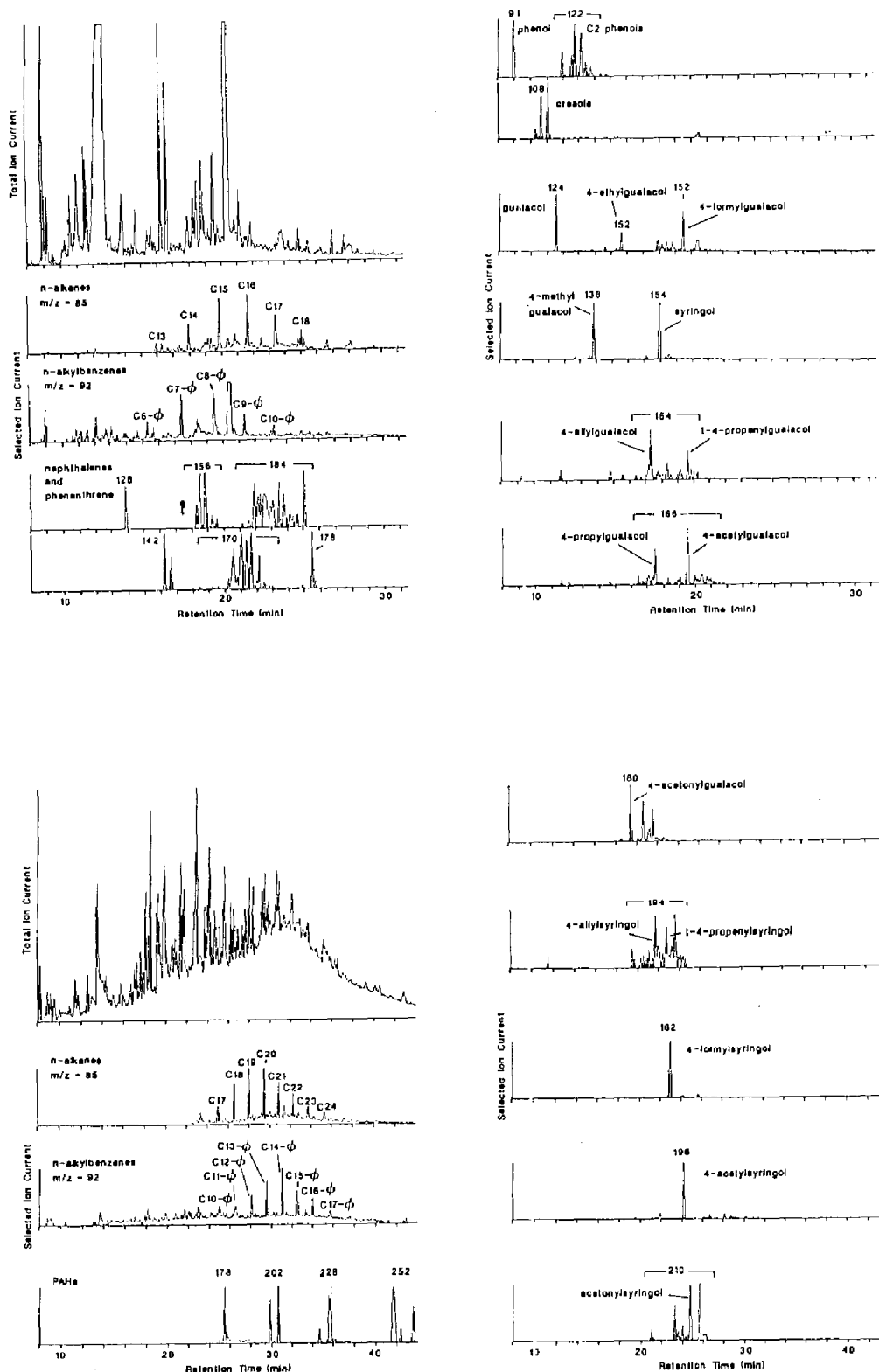


Figure 1: GC/MS analysis of the unfractionated PUF (top) and filter (bottom) extract from a 12 hour PM-10 Hi-Vol collection of urban air in a residential neighborhood. Although the total ion current chromatograms are complex, the selected ion chromatograms clearly show organic pollutants from vehicle exhaust (n-alkanes, n-alkylbenzenes, and PAHs) as well as organics from wood smoke including guaiacol and syringol derivatives. The numbers above the chromatographic peaks indicate the mass used for the selected ion plots.

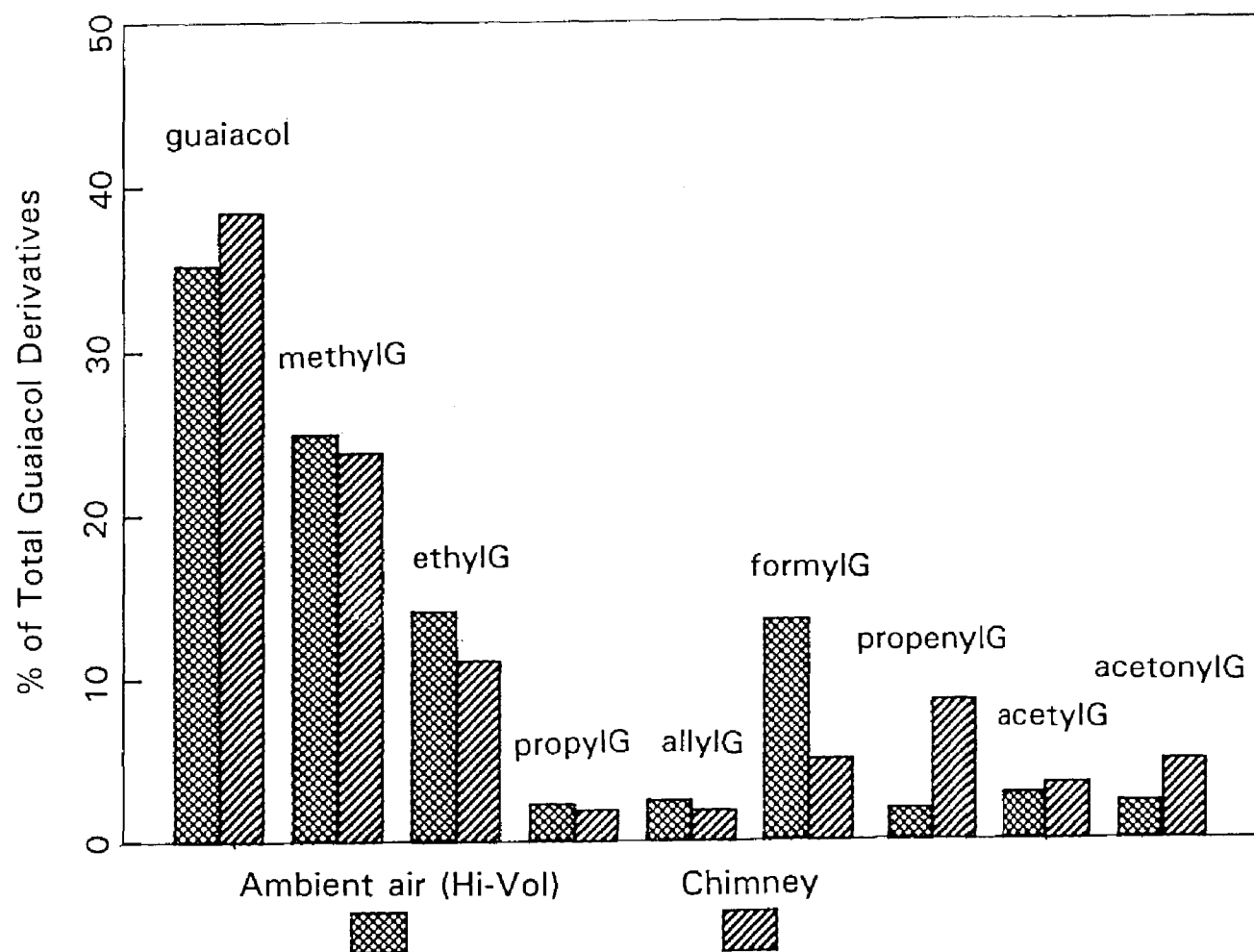


Figure 2: Relative average concentrations of individual guaiacol derivatives collected in urban winter air and from the chimneys of 28 different wood stoves and fireplaces.

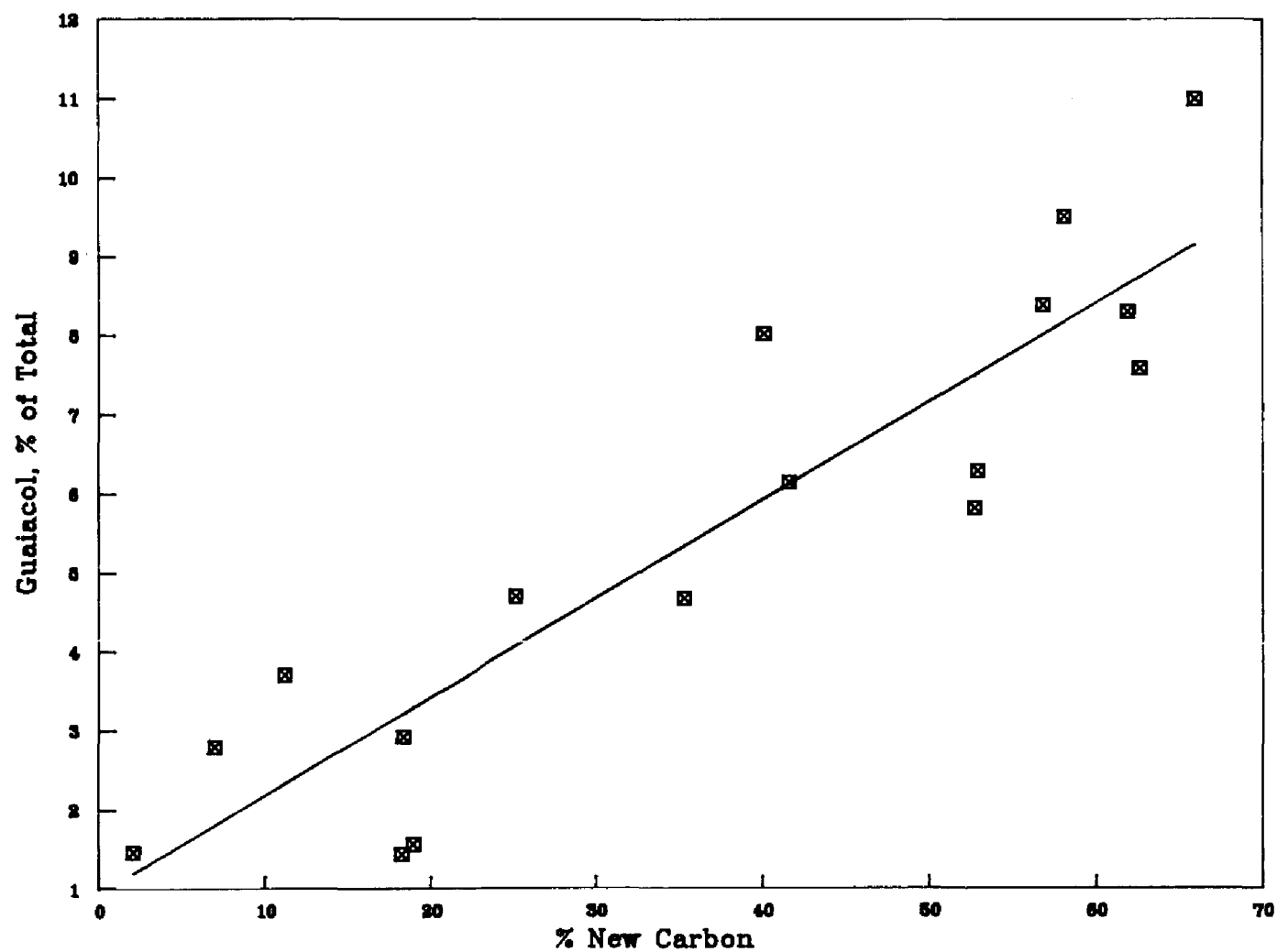


Figure 3: Correlation of % guaiacol (compared to total organics quantitated) collected from the Hi-Vol winter air samples with the fraction of "new" particulate carbon based on ^{14}C analysis.

SOLID SORBENT AIR SAMPLER FOR THE CHARACTERIZATION
OF CONTAMINANTS IN SPACECRAFT ATMOSPHERES

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Assessment of air quality aboard the Shuttle during early missions was trusted to daily 300 ml. grab samples acquired with evacuated stainless steel cylinders. Additionally, a small sample of the charcoal used to scrub the cabin air as part of the Environmental Control and Life Support System (ECLSS) was analyzed by gas chromatography/mass spectrometry following thermal desorption and cryotrapping.

In later missions the number of sample cylinders manifested was reduced such that daily grab samples were no longer possible. This, combined with the greater number of compounds detected in the charcoal samples, led to the development of the Solid Sorbent Air Sampler (SSAS) by the Biomedical Operations and Research Branch at the Johnson Space Center.

This paper will present a detailed description of the SSAS which is capable of acquiring eight 24-hour composite samples with minimal crew involvement. The entire system, which is battery operated, is contained in a cylinder of only 4.5" diameter x 8 " length. Furthermore, each of the eight Tenax sampling tubes can be desorbed without exposing the adsorbent to the laboratory atmosphere. Results from Shuttle missions will be presented to demonstrate the effectiveness of the SSAS in characterizing the internal cabin atmosphere.

Introduction

The enclosed environment of a spacecraft, like any partially closed atmospheric system, is prone to the accumulation of volatile organic compounds (VOCs). Some of these volatile organic contaminants arise from the familiar terrestrial sources: human metabolic products, materials offgassing, leaks and/or spills of onboard chemicals, clothing, foods, hygiene products, thermodegradation of synthetic materials, and fire extinguishant. Sources of VOCs unique to spacecraft include: the Environmental Control and Life Support System (ECLSS) and extravehicular activities (EVA). The analysis of charcoal taken from the ECLSS atmospheric scrubbing system during the Apollo flights demonstrated the presence of numerous VOCs in the spacecraft atmosphere.¹ Although the concentrations of most VOCs were below 1 part per million (ppm), crew safety was still a concern given the physiological changes that occur in space and the uncertainties associated with long-term exposure to low concentrations of VOCs.

Efforts to define a sampling and analytical method capable of detecting sub ppm levels of volatile organic contaminants drew heavily from accepted air sampling methods of the time² and led to the development of an atmospheric volatile concentrator for Skylab³ and the Air Sample Assembly (ASA) for Shuttle. Both systems employed Tenax-GC as a medium upon which VOCs were trapped from the spacecraft's internal atmosphere during flight. These archival samples were subsequently returned to Earth and analyzed. Cross-contamination of tubes, tube contamination during ground analysis, and excessive crew time for sampling were a few of the disadvantages of these devices which produced less than satisfactory results.⁴ Complimenting the adsorbent-based sampling technology on Shuttle was the collection of 300 ml grab samples in evacuated stainless steel cylinders each flight day. Increasing demands on payload volume and weight requirements have resulted in reducing the sampling protocols to a pre-flight sample and a single inflight sample collected the last day of a mission. Additionally, the grab sample is a single point in time and space; therefore, it may not be a true representation of the atmosphere over the entire mission.

The development of a new sampling device, which eliminated the problems observed in previous efforts, culminated in the construction of the Solid Sorbent Air Sampler (SSAS). The SSAS is a compact, lightweight unit capable of collecting seven 24 h composite air samples. The eight air samples, each representing a volume of 3 liters pulled over Tenax-GC adsorbent, can be collected using 4 "C" cell alkaline batteries. Additionally, an entire sampling procedure, including laboratory analysis, can be completed without exposing the Tenax tubes to a contamination source. Furthermore, crew time required to obtain the samples is less than one minute per day.

This paper will describe the design and operation of the Solid Sorbent Air Sampler, and present results from data collected during Shuttle missions. The SSAS, being a compact, easy to operate, quiet sampler, can also be applied to studies of indoor air quality.

Experimental Methods

The success of the Solid Sorbent Air Sampler can be traced to its simplicity (Figure 1). The SSAS is housed in a metal cylinder (anodized aluminum) 4.5" in diameter and 9.5" in length with a total weight of 4.25 lbs. It is composed of two subassemblies: an electronic assembly and a gas flow assembly. The electronic subassembly contains a battery pack, a diaphragm pump (model 11-0002, AeroVironment, Inc., Pasadena, CA), and a timing circuit that pulses the pump, thus permitting a sampling rate of

approximately 3 liters/24 h. An ON/OFF switch is available to activate and deactivate the pump. The heart of the gas flow assembly is an 18-port (1/32" fittings) microvalve (Valco, Houston, Tx.) that connects the inlet and outlet of all eight glass-lined Tenax tubes, the sample inlet, and the pump. The sample inlet and the inlet/outlet ports of the Tenax tubes all have 1 mm screen filters to eliminate particulate clogging of the inlet and prevent loss of Tenax. Each 1/4" O.D. [.158" (4mm) I.D.] x 5.91" (15 cm) glass-lined tube (SGE, Inc., Austin, Tx.) contains 0.5 grams of Tenax-GC (Alltech, Deerfield, IL.). The valve rotates easily through eight positions indicated by the inscribed numbers (1-8) on the top of the unit. If the valve is pointing to #1, then the sample inlet, the inlet and outlet of tube #1, and the pump are in line; and, a sample of air is being pulled across the Tenax in tube #1 by the pump. When the valve is facing #2, then tube #2 would likewise be in line and an air sample would be collected in that tube.

The sampling procedure is brief and can easily be written on a small label attached to the unit and still leave space for recording sampling times. Since an "in line" Tenax tube is exposed to the environment even when the pump is deactivated, the valve is always positioned on Tube #8 when the SSAS is not operating. Consequently, samples collected on Tube #8 will be of dubious value because of volatile organics diffusing in and out of the tube from the surrounding environment. The three steps required to initiate a seven day sampling cycle with the SSAS are: switch the unit "ON" to start the pump, turn the valve to the first sample tube (usually #1), and record the start time. At the end of a specified sampling period, the user manually switches the valve to the next Tenax tube and records the time. At the conclusion of the sampling operations, the valve is again switched to position #8, the time is recorded, and the SSAS is deactivated by switching the unit to "OFF". The SSAS unit can now be sent to a laboratory for analysis without further preparation since initial testing on the unit demonstrated no cross-contamination between tubes.

Once the Solid Sorbent Air Sampler is received in the laboratory, the electronic subassembly is removed and a helium purge line is connected to the pump line. The sample inlet, with the filter removed, is attached to a valve on a gas chromatograph leading to a cryotrap, and the SSAS valve is positioned so that the tube to be desorbed is in line. The tube is then heated to 200°C for 20 minutes with a 20 cc/min helium flow over the Tenax, while the cryotrap is held at liquid nitrogen temperature. A flow diagram of the gas chromatograph inlet system is shown in Figure 2. At the conclusion of the desorption process the cryotrap is heated and VOCs are transferred onto a GC column where subsequent GC/MS analyses are performed to obtain qualitative and quantitative data. Each tube is desorbed in a similar manner with a total run time of two hours per tube. Once the desorption process is completed, the SSAS unit is attached to another source of helium flowing at 10 cc/min and each tube is "cleaned" for 24 hours at 250°C. Following this cleanup procedure, a blank is run on each tube, and, with satisfactory results the unit is again ready for use. It is noteworthy that the entire protocol is performed without removing the Tenax tubes from the SSAS unit; thereby, eliminating a potential contamination step.

Results

The Solid Sorbent Air Sampler has been restricted to Shuttle missions that either contain the Spacelab or involve the first flights of new or extensively refurbished vehicles. These restrictions have limited the inflight operation of the SSAS to seven missions over the past five years. Unfortunately, the archival samples collected have been analyzed on a variety of GC/MS instruments. However, some trends in the data do surface and with the SSAS manifested on several missions scheduled for the

near future, a more comprehensive characterization of the Shuttle internal atmosphere should be forthcoming.

The results presented in Table I^{5,6} indicate that the total mass of volatile organic compounds collected is generally in the range of 1.5 to 2.5 mg/m³. As noted, these data do not include the contributions from ethanol and 2-propanol because these compounds are introduced into the cabin atmosphere at inordinately high levels by hygiene and medical wipes respectively. The concentration of ethanol rises dramatically, especially near the conclusion of mission, when housekeeping activities usually increase in anticipation of the return to Earth. The total mass of volatile organics collected on Tube #7 of STS 32 was 5.5 mg/m³; however, ethanol and 2-propanol contributed 3.6 mg/m³. Subtracting the contributions of the ethanol and 2-propanol leads to the observation that the concentration of VOCs appears to stabilize and rises only slightly with time during a mission.

The data presented in Table II⁷ illustrate several important points. First, the distribution of volatile organic compounds in the spacecraft atmosphere is substantially different from that typically found in an indoor environment on Earth. Terrestrial samples of indoor air usually contain as high as 80%-90% hydrocarbons (alkanes, alkenes, etc.).⁸ As noted in Table II, the spacecraft atmosphere contains more oxygenated hydrocarbons and halogenated compounds than alkanes, alkenes, and aromatics. This composition may reflect careful materials selection and rigorous offgas testing applied to all nonmetallic substances under consideration for use in flight hardware. Although offgassing of materials in flight still occurs, the major contributors to the VOCs in the atmosphere seem to be from metabolic processes and utility chemicals. A second point to be ascertained from Table II is that this air sampling technique can indicate a problem has occurred or the success of a correction effort. For example, the levels of halogenated hydrocarbons which were fairly high in the pre-Challenger era (3 flights with the SSAS), appear to have been reduced. Furthermore, in the post-Challenger era (4 flights with the SSAS) the level of silicone compounds would appear to be remarkably high; however, this can be traced to an anomaly on board a single mission (STS 28). Finally, in spite of different sampling devices, personnel, and analytical systems, the trends of VOC composition in spacecraft atmosphere appear to be consistent throughout the entire 17 years since Skylab.

Conclusion

The Solid Sorbent Air Sampler has proven to be a valuable means of collecting volatile organic compounds from the Shuttle atmosphere for subsequent ground analysis. The ability to collect, analyze, and clean each tube without exposing the Tenax to the atmosphere is an important advantage of this device. The SSAS has provided information on the character of the volatile organics in the Shuttle atmosphere in both the ppm and sub ppm ranges. The analyses of the SSAS samples and appropriate trend analysis are tools that can be employed to identify anomalies or modifications in the Shuttle atmosphere. Facing the challenges presented by long duration missions, such as Space Station, necessitates exploring the potential of multi-sorbent tubes and automated valve switching to meet the demands of extended spaceflight. Additionally, studies comparing the SSAS with Passive Sampler Devices (PSDs) is a high priority in the search for sampling strategies for Space Station. Moreover, the design features of the SSAS for spaceflight (lightweight, compact, quiet, simple operation, and inexpensive) are the very same attributes required for a successful indoor air sampler intended for long-term, broad base studies on Earth.

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TABLE I. TOTAL VOLATILE ORGANICS
COLLECTED (mg/m³)*

MISSION	SOLID SORBENT AIR SAMPLER TUBE NUMBER							
	1	2	3	4	5	6	7	8
STS-51B	4.1	3.1	11.6					
STS-51J	1.4	1.4	1.3	1.7	1.2	1.7	1.0	
STS-61A	2.9	1.9	2.0	2.4	2.2			
STS-26	0.6	0.4	.81					
STS-27	2.3	2.3	1.8	2.3				
STS-28	2.3	1.6	1.6	1.8	1.2			
STS-32	1.0	0.8	1.5	1.5	1.5	1.5	1.9	2.0
* mg/m ³ OF ETHANOL AND 2-PROPANOL ARE NOT INCLUDED IN THESE VALUES								

**Table II. COMPARISON OF AVERAGES FOR VOLATILE
ORGANIC COMPOUND CLASSES IN
SPACECRAFT ATMOSPHERE BY ERA**

MISSIONS	COMPOUND CLASS			
	ALKANES ALKENES AROMATICS	KETONES ALDEHYDES ALCOHOLS ESTERS	SILICONE COMPOUNDS	HALOGENATED HYDROCARBONS
SKYLAB*	12.5**	42.5	3.0	32.5
PRE - CHALLENGER	8.4	41.3	2.9	47.4
POST- CHALLENGER	7.0	50.1	22.7	20.2
* AN ESTIMATED AVERAGE ** ALL VALUES ARE mg/m ³				

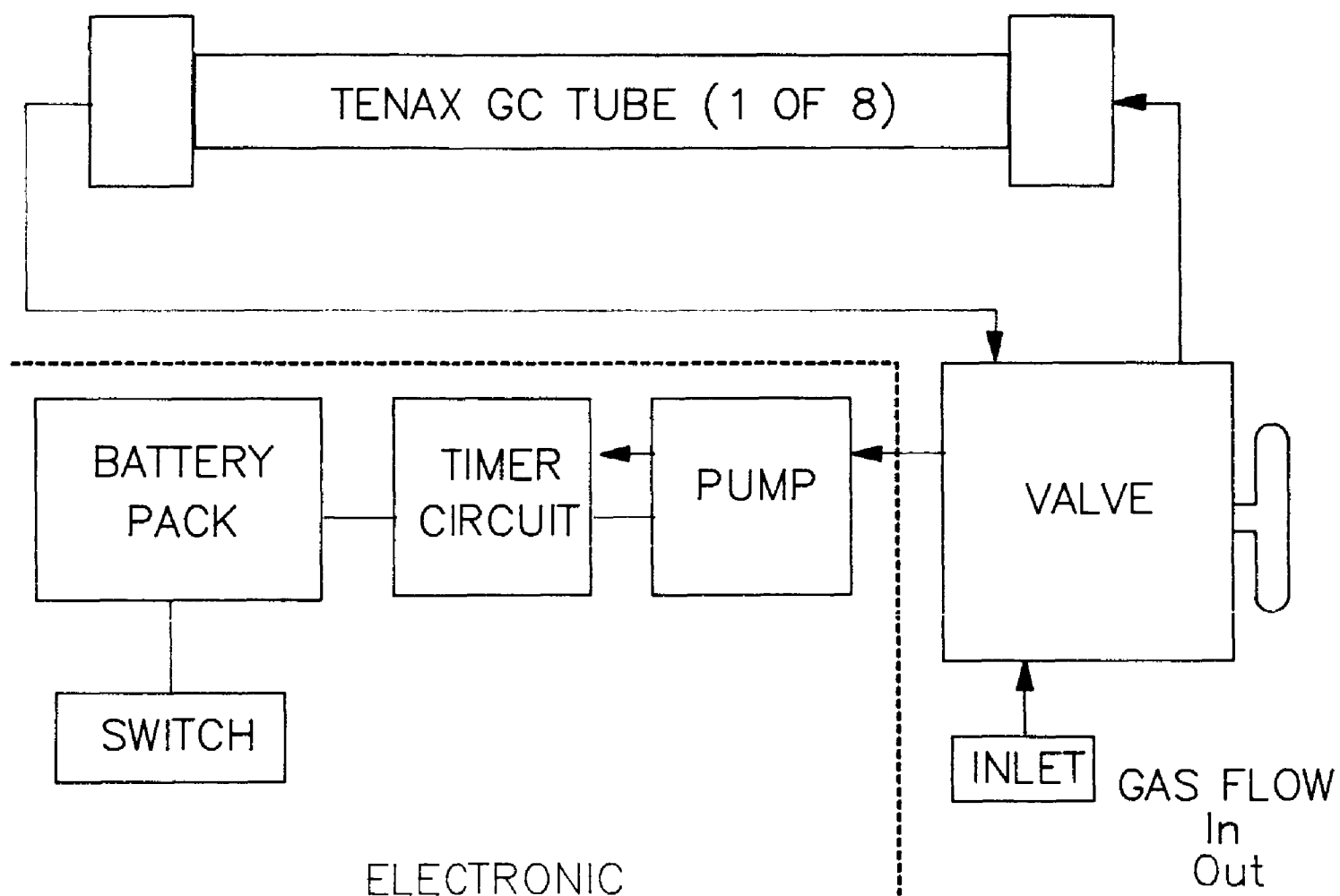


Figure 1. Schematic of the solid sorbent air sampler electronic and gas flow subassemblies. Arrows indicate the flow of an air sample through the sampler.

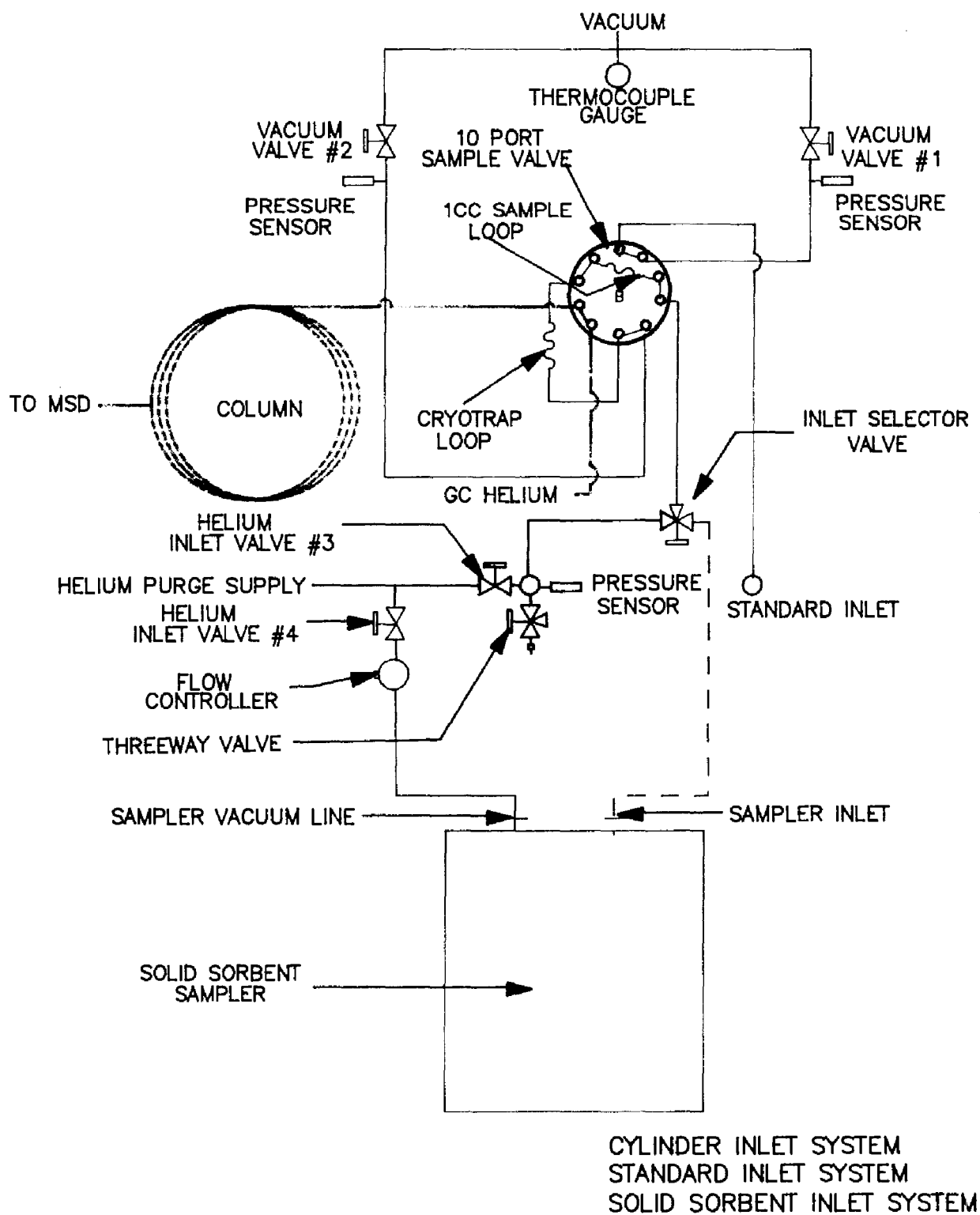


Figure 2. GC/MSD system valving and inlet paths showing the sample valve in position for cryotrapping.

SULFUR ON SURFACES OF ATMOSPHERIC MINERALS
AND SPORES

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Atmospheric particles were analyzed by electron microscopy to obtain direct evidence for S enrichment on minerals and spores in the 0.5 to 10 μm diameter range. The particles were collected at Research Triangle Park for two weeks during summer, 1988, using dichotomous samplers that were modified for use with electron microscopy. One of the samplers was equipped with an annular denuder that removed acidic gases upstream of the filters to avoid artifact reactions on the filter between gases and particles. A comparison of X-ray spectra for atmospheric particles and locally collected soil and mushroom spores revealed significant S-enrichment of atmospheric silicates and spores. It was concluded that the S enrichments were caused by atmospheric reactions and not by sampling artifact.

Introduction

The goal of this study is to obtain direct evidence for enrichment of sulfur on minerals and spores in the atmosphere as a function of diameter in the 0.5- to 10- μm range. To meet that goal, we compared ambient particles with locally collected soil particles and mushroom spores. To avoid confusion about whether some of the observed sulfur enrichment is caused by SO_2 reacting with particles on the filter during sampling, we analyzed samples from a second simultaneously operated dichotomous sampler that was equipped with an annular denuder that removed SO_2 upstream of the filters. Instead of using standard dichotomous samplers, which collect fine particles as multiple layers that are unsuitable for microscopy analysis, we used modified dichotomous samplers that collect fine and coarse particle samples that are suitable for both microscopy and bulk sample analysis¹. We used X-ray fluorescence (XRF) to obtain the elemental content of the samples and scanning electron microscopy (SEM) with an energy dispersive X-ray (EDX) spectrometer to analyze individual fine (<2.5 μm aerodynamic diameter) and coarse (2.5 to 10 μm) particles.

Methodology

Ambient particles were collected simultaneously in two modified dichotomous samplers¹, placed on the roof of EPA laboratory 10 m above ground in Research Triangle Park, NC, for 10 consecutive 24-h periods between June 28 and July 9, 1988. One of the samplers was equipped with an annular denuder² to remove SO_2 , HNO_2 and HNO_3 .

All of the Teflon filters (coarse and fine) were analyzed by gravimetry for mass and by XRF. Several coarse Teflon and fine Nuclepore filters were analyzed manually in a SEM equipped with an EDX spectrometer. Size, X-ray spectrum and morphology were recorded for several hundred particles.

Soil and road dust, and fresh mushroom spores from the area were sampled on Teflon and Nuclepore filters. The Teflon filters were analyzed by gravimetry and XRF, the Nuclepore filters by SEM-EDX.

Results and Discussion

Source sample analysis

Spores. The three major elements detected by XRF are P, S and K, and the S/P and S/K ratios are about 0.4 and 0.5, respectively. Such ratios for spores are similar to results reported for pollen³.

Figure 1 is a SEM micrograph and an X-ray spectrum of mushroom spores. The spores are quite uniform in size and shape. The spores contain P, K, and S with ratios of 0.3- 0.4 and 0.7-0.8 for S/P and S/K, respectively.

Soil and Road Dust. SEM analysis of soil and road dust sample showed that particles were irregular in shape and composed mostly of silicate minerals. Sulfur was not associated with these minerals. Only few particles analyzed in the microscope had detectable amounts of S.

XRF results for ambient samples

The mass and the complete set of XRF data for fine and coarse particles led to the following findings:

(a) The total particle mass concentration ranged from 20 to 50 $\mu\text{g}/\text{m}^3$, and the ratio of fine to coarse mass concentrations ranged from 1.3 to 5.3.

(b) Sulfur, as ammonium sulfate, accounts for about 50% of the fine mass concentration. No other element (>5%) was measured by XRF. Sulfur was detected by XRF in the coarse fraction although the concentration was low.

(c) Alumino-silicate minerals account for about 50% of the coarse mass. Volatile nitrates, spores, other organic material, and water can contribute to both size fractions but were not measured by XRF.

(d) Day to day variations in mass and elemental concentrations are as large as a factor of 2 for consecutive samples. The relative changes in the coarse particle composition are not identical to those of the fine fraction.

(e) Particle losses in the annular denuder were very small.

Three cases were chosen for SEM-EDX analysis based on S in fine fraction and Si (minerals) in the coarse fraction:

Case I (June 28): low fine S and nearly median Si,

Case II (July 3): high fine S and lowest Si and

Case III (July 5): lowest fine S and high Si.

Case II represents S concentrations that are typical of summertime conditions in the East and Midwest, and cases I and III represent conditions of unusually low S-concentrations in the eastern United States.

SEM results for ambient samples

Coarse particles, analyzed by SEM-EDX, were classified into categories according to morphology and X-ray spectrum^{1,4}. Table 1 shows particle counts in each category. For the above three cases particles consisted of 60 - 80% minerals, 10 - 30% spores and pollen, and 1 - 2% fly ash.

Almost all fine particles smaller than 0.5 μm were sulfates. The non-sulfate fine particles, 0.5 to 2.5 μm , were 50-60% organics, 30-45% minerals, 5-10% spores, and 0 - 3% fly ash.

S enrichment in ambient samples

Figure 2 show SEM-EDX X-ray spectra of atmospheric silicates and spores that appear to be enriched in S relative to the spore and mineral source samples. To systematically characterize particles according to S enrichment, coarse fraction silicates and spores were classified as follows:

$N_s < 150$	-	no S enrichment
$150 \leq N_s < 350$	-	some S enrichment
$350 \leq N_s$	-	high S enrichment

where N_s is the number of S X-ray counts acquired in a 30-s analysis. Fine fraction silicates and spores were classified similarly except that the count limits were 30% lower than those shown above. On the basis of these definitions of S-enrichment, all the fresh spores and soil minerals (see Figure 1), are in the category of "no enrichment".

What is the cause of the S-enrichments in atmospheric particles? First, we eliminate the possibility that SO_2 reacted with particles on the filter during sampling because the denuder in one of the samplers removed SO_2 upstream of the filter. The small differences between denuder and non-denuder data in Table 1 are due to counting statistics and cannot be attributed to the denuder. Second, our use of modified dichotomous samplers caused particles to be spaced far enough apart on the filter so that each X-ray spectrum are representative of only the particle being examined. Third, the silicates and spores in our source samples were not enriched in S.

Thus, we conclude that the observed S-enrichments are a consequence of reactions that occur in the atmosphere while particles are airborne. A

possible mechanism is that SO₂ and oxidants diffuse into and react in a water layer that forms on particles in clouds and at high humidity.

Data in Table 1 indicate that S-enrichment occur in all three cases studied for coarse and fine particles. The amount of enrichment was greatest for case II, which represents typical summertime high fine S concentrations, and was least for cases I and III.

Summary and Conclusions

The main results are summarized in the following:

(1) No significant difference in the S-content of atmospheric spores and silicates was obtained for samples collected with and without a denuder. Thus, there is no evidence for gas-particle reactions occurring on the filter during sampling.

(2) The sources analyzed (soil and spores) were not enriched in S. Sulfur was not detected by XRF in the soil minerals. Sulfur was found in spores as part of their intrinsic composition but was always less than the amount of P and K in each spore studied.

(3) All ambient samples that we analyzed by SEM-EDX contained silicates and spores that were enriched in S. Moreover, on July 3, a day when S concentrations were typical of Eastern summertime values, most of the silicates and spores were either enriched or highly enriched in S. The S-enrichments were caused by atmospheric reactions. Although this study demonstrated that both fine and coarse fraction minerals and spores become enriched in S while airborne, it does not determine the mechanism by which this happens.

Acknowledgements

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Table 1. Particle count by category for coarse particles in the 1.5- to 10- μm diameter range *

	Case I: June 28		Case III: July 5		Case II July 3	
	no denuder	denuder	no denuder	denuder	no denuder	denuder
Silicates						
No S enrichment	30	37	67	45	11	7
Some S enrichment	29	11	12	21	24	24
High S enrichment	4	6	5	7	18	34
Spores and pollen						
No S enrichment	15	13	4	4	3	4
Some S enrichment	11	12	4	2	4	7
High S enrichment	14	13	5	5	16	11
Others #	17	25	16	23	24	30
Total	120	117	113	107	100	117

* The total area scanned in four fields was 38000 μm^2 per sample.

Include other minerals, fly ash, organics, and metal rich particles.

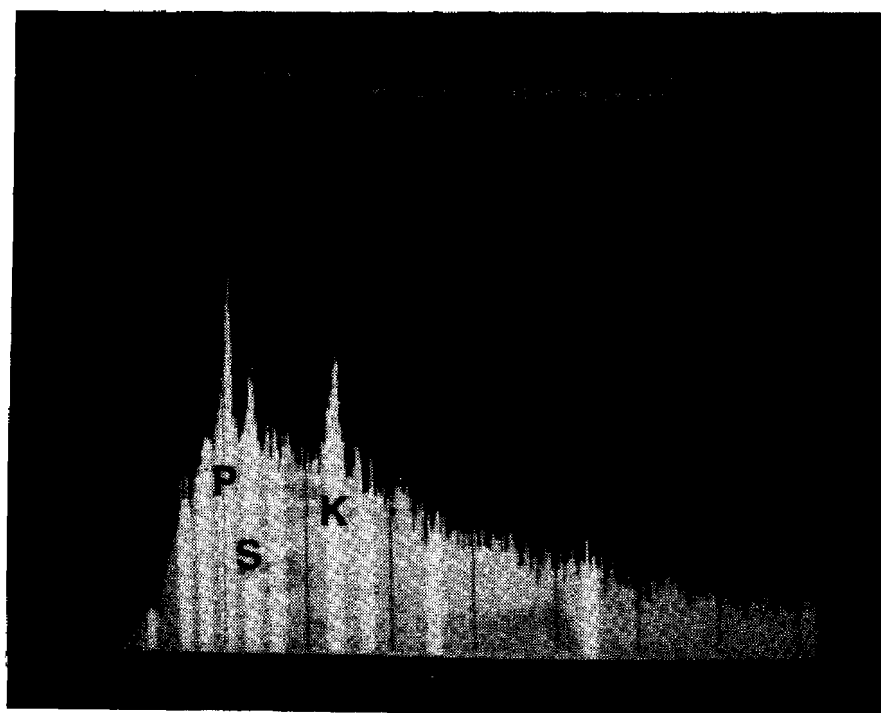
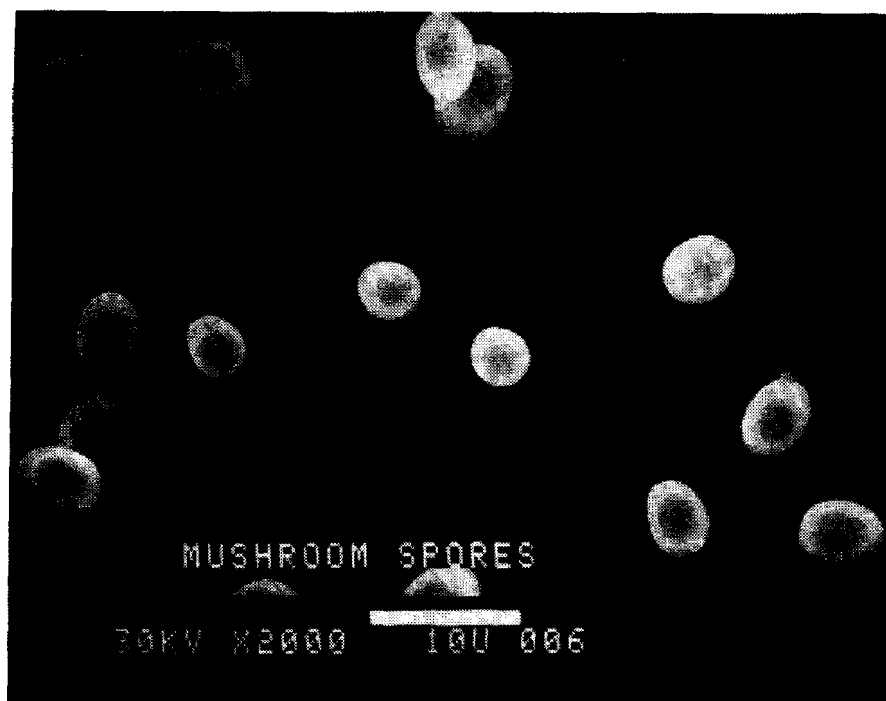


Fig. 1. (A) Micrograph of mushroom spores at X5000 magnification. (B) X-ray spectrum of typical mushroom spore. Note that the S peak (abundance) is lower than that of P or K.

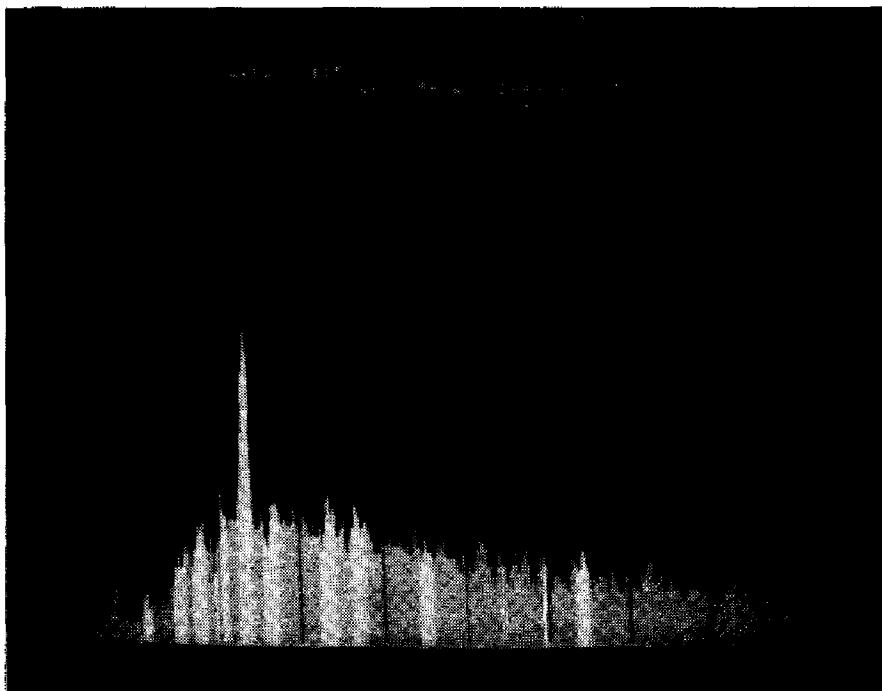
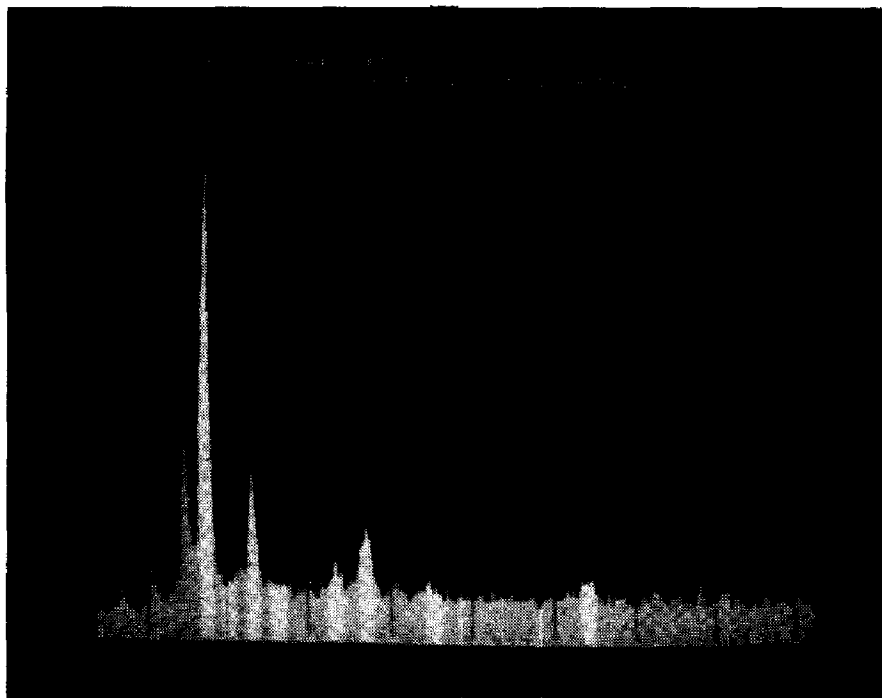


Fig. 2. X-ray spectra of coarse particles enriched in S (cursor line is on the S peak) in July 3 samples: (A) mineral (major peaks are Al, Si) and (B) spore (high background spectrum characterizes biological material) from sample with no denuder.

DEVELOPMENT OF ATMOSPHERE GENERATION, MONITORING, AND CLEAN-UP SYSTEMS FOR ACID AEROSOL ANIMAL EXPOSURES

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The subchronic effects of ambient levels of acid aerosols has yet to be determined, due mainly to the highly reactive nature of these compounds. This paper explains the development of an acid aerosol exposure system for animals. The animal chambers are continuously monitored and maintained for the proper aerosol concentration, temperature, relative humidity, and air changes. The quality of aerosol delivered is determined by the aerosol generation system. The generation system was composed of a constant output atomizer (TSI, Inc.), which was linked to a diffusion dryer, aerosol neutralizer, and heat exchange tee. To maintain a uniform aerosol distribution, the Hazleton 2000 Inhalation Chamber was used to house the animals. Continuous monitoring was accomplished by use of a sulfur analyzer and a tapered element oscillating microbalance (TEOM)³ linked to each chamber. Aerosol species identification and characterization was determined by annular denuder samples analyzed by ion chromatography (IC). The aerosol particle size was determined by use of cascade impactors and particle-sizing instruments. Each chamber effluent was conditioned by a scrubber (Mystaire) for removal of acid aerosols and gases before being exhausted to the atmosphere. The design of these systems provides the operator with a high degree of freedom to accomplish routine analysis of chamber samples while continuously maintaining four inhalation exposures.

Disclaimer

This is an abstract of a proposed presentation and does not necessarily reflect EPA policy.

Introduction

The term acid aerosols includes many acid species, including two sulfated species – H_2SO_4 and NH_4HSO_4 , which are both droplets in ambient air. Although HNO_3 is considered an "acid gas" because of its ability to form a gas molecule from aqueous solutions, in dilute aqueous solution (0.1 M), HNO_3 is strong, being about 93% dissociated¹. This indicates that an aerosol generator will deliver HNO_3 as an aerosol and gas mixture.

The subchronic effects of ambient levels of acid aerosols (H_2SO_4 , NH_4HSO_4 , and HNO_3) have not been examined thoroughly using state-of-the-art measurement and exposure techniques. This paper describes the development of an acid aerosol inhalation exposure system for guinea pigs. The exposure chambers provide the animals with the proper temperature, relative humidity, and adequate ventilation. The exposure system was developed to deliver predetermined concentrations of acid aerosol within a specific particle size range (0.4 to 0.8 μm mass median aerodynamic diameter [MMAD]); to minimize acid neutralization by NH_3 ; measure the aerosol concentration continuously and quantitate the different chemical species present, and exhaust chamber effluents that are essentially acid free.

Methods

Generation

The aerosol generation systems for each test material (H_2SO_4 , NH_4HSO_4 , and HNO_3) are described below. These systems provide stable, accurate test agent flow rates to the exposure chambers to provide target aerosol concentrations and aerosol particle size.

The generation equipment is mounted on a 3 ft wide by 4 ft long by 2 in. thick platform mounted to the wall and ceiling 6 ft above the floor, and includes metering pumps, constant output atomizers, diffusion driers, and particle neutralizers. These items are available commercially. A solution of either H_2SO_4 , NH_4HSO_4 , or HNO_3 is metered into a nebulizer and atomized as a polydispersed aerosol, with the excess solution being delivered to a waste reservoir. The aerosol becomes more uniformly sized by the removal of excessive moisture in the diffusion dryer. The mechanical action of generators can create highly charged aerosols². These electrical charges are neutralized to a normal Boltzmann equilibrium by passing the aerosol through a particle neutralizer (2.0 mCi of ^{85}Kr). Finally, the aerosol is delivered to the exposure chamber through a diluter tee to prevent aerosol loss and ensure proper mixing with the chamber supply air. The initial aerosol particle size is determined primarily by the acid solution concentration delivered to the nebulizer. Final aerosol particle size is influenced by chamber humidity and temperature. The exposure chamber concentration is controlled by the metering pump and chamber air flow rates.

Monitoring and Control

During operation of the acid aerosol exposure facility, all inhalation chambers are monitored continuously and have automatic control and alarm for temperature ($73 \pm 3^\circ\text{F}$), relative humidity ($60 \pm 10\%$), and chamber air flow (minimum 15 air changes/h). In addition, the exposure chambers are monitored continuously for contaminate flow rate (within 1% of actual flow rate), chamber static pressures (between negative 0.1 and 0.5 in. H_2O), and nominal concentrations ($\pm 10\%$). These three parameters are controlled manually.

The chamber NH_3 levels are monitored on a routine basis before the start of every daily exposure. This procedure includes sampling every chamber by drawing a known volume of chamber atmosphere through an impinger and analyzing the sample with an NH_3 analyzer. Once the NH_3 levels in each chamber are acceptable (less than 20% neutralization of target acid concentration), all exposures begin simultaneously. An NH_3 probe is used to verify the NH_3 analyzer operation on a routine basis.

Acid aerosols generated are monitored in the exposure chambers for particle size distributions and total particle concentrations. To ensure complete aerosol size determinations, two instruments with overlapping particle size ranges are used to determine the aerosol particle distribution. An electrical aerosol analyzer ([EAA] TSI, Inc.) is dedicated to each exposure chamber and one optical particle analyzer (Climet, Inc.) is used for confirmation and quality assurance (QA) of each EAA. Each exposure chamber will be monitored continuously for particle size distributions to ensure that uniform aerosols are generated during the entire exposure period. Aerosol mass concentrations will be analyzed by a tapered element oscillating microbalance (TEOM)³ ambient particulate monitor (Rupprecht & Patashnick Co, Inc.). This analyzer enables precise and accurate measurement of all aerosols in the chamber as on-line, real-time data. These data provide the operator information helpful for precise control of the generation system, as well as continuous aerosol mass concentration analysis. One analyzer will be dedicated to each exposure chamber to provide on-line, real-time aerosol concentrations.

The speciation determination during acid aerosol exposures is essential because of the highly reactive nature of these aerosols and trace NH_3 levels created continuously by the animals. EPA method IA09, using annular denuder system (ADS) followed by IC analysis, will be used to speciate the aerosol in the exposure chambers (EPA Method IA09, draft). This system was developed to measure reactive acidic and basic gases and particulate matter which are contained in indoor ambient air. The following chemical species can be measured by the ADS: gaseous SO_2 , HNO_2 , HNO_3 , and NH_3 and particulate SO_4^{2-} , NO_3^- , NH_4^+ , and H^+ . Other similar chemical species can be collected successfully with just a few simple modifications (i.e., changing the denuder coating solutions). Once collected, the species concentrations are quantified by IC analysis and/or NH_3 analyzer. The ADS sampling is performed once a day on every exposure chamber to monitor for changes in chamber atmosphere species. All NH_3 analyses were performed with an NH_3 probe (Fisher Scientific) in 20 mL of deionized water. The samples were collected for 30 to 60 min with a midjet impinger.

The total sulfur in the exposure chambers also is determined using an on-line real-time total sulfur analyzer. This analyzer is multiplexed between all acid aerosol exposure chambers for quality control over sulfur species (SO_4^{2-} , SO_2).

Chamber Systems

Hazleton 2000^{4,5} whole-body inhalation exposure chambers are used to conduct the animal exposures (Figures 1 and 2). The 2.0-m³ chambers are constructed of stainless steel and glass and are designed for animals to live in the chambers⁵. Each chamber contains six cage modules with integral food troughs and automatic watering. Catch pans are mounted below each cage module to collect the animal waste products. The animal caging capacity is 60 guinea pigs per chamber. All chamber air is filtered first by a prefilter, then by a bed of activated carbon. The incoming air is then humidified to ~60% RH and is passed through a bed of Type CA charcoal, two beds of Purafil®, and finally a high-efficiency particulate air (HEPA) filter. This has proven to be an effective method of removing ambient NH_3 . The supply then is dehumidified and rehumidified to ~50% RH. This conditioned supply air is delivered to a plenum maintained at 1.0 in. positive pressure which supplies all inhalation chambers. The exhaust air system has redundant exhaust blowers. When a mechanical failure occurs, the system automatically switches over to the backup blower without loss of exhaust air flow.

The chambers are operated to minimize the neutralization of the H_2SO_4 by NH_3 forming $(\text{NH}_4)_2\text{SO}_4$. This situation is addressed by maintaining strict cleanliness in the exposure chambers. To maintain the lowest NH_3 levels possible, animals are exposed in one set of chambers for 4 h, then they are transferred to a second set of chambers (or filtered clean racks) for holding overnight. Exposure chambers are cleaned so as to remove the animal waste products splattered on the cages and chamber walls which are not removed by simply replacing the drop pans and cage boards after exposures. Preliminary data collected from the proposed exposure facility indicate that the above procedures are a necessary first defense in the effort to minimize the NH_3 problem. The average NH_3 concentrations for 30 rats in the Hazleton 2000 chambers (15 air changes/h) with no control measures ranges from 0.2 to 1.0 ppm, depending on

the number of hours the animals are housed in the same chamber. The same analysis has been run for 30 guinea pigs, with the average NH_3 ranging from 0.5 to 1.5 ppm.

Aerosol Distribution

Aerosol distribution of H_2SO_4 in the Hazleton 2000 has been studied⁴. Additional distribution testing will be conducted in the exposure chambers prior to initiating the proposed animal exposures for toxicological evaluation. A TEOM will be used to monitor the concentration in the exposure chamber after the aerosol generator has stabilized. A reference position and several points will be selected that are located in the breathing zone of the test animals. The sample probe of the aerosol mass monitor will be rotated through the selected sampling positions allowing sufficient time for the sample to stabilize at each position. The data will be analyzed by a statistician for temporal and spatial variability. The aerosol distribution will be evaluated thoroughly at all dose levels, then spot checks will be performed on the remaining exposure chambers to verify the performance of each chamber.

Waste Disposal

The removal of acid aerosol-laden atmospheres from the inhalation exposure chambers is accomplished with a wet scrubber (Mystaire, Heat Systems, Inc.). This device physically removes the aerosol particles from the air with water from a high-pressure nozzle sprayed on a nylon mesh. The water is recirculated through a 10-gal holding tank mounted beneath the pump. Acidified water is removed, neutralized, and replaced on a regular schedule. (Figure 2).

Results

Current research on the neutralization of NH_3 , which is created by the test animals (rats and guinea pigs) and is present in ambient air, indicates a significant problem with whole-body exposures. The reactive nature of NH_3 can only be controlled by complete neutralization of it as it is formed.

The most significant sources of NH_3 is the animals themselves, from action of urease bacteria from animal feces on the urea found in the urine⁶, and from the expired air.⁷ The results of the NH_3 levels of rats vs. guinea pigs are shown in Table I. The current control methods include using chambers coated with 0.1N H_2SO_4 solution applied with an aerosol generator for 2 h and allowed to dry overnight before loading the animals. The use of neomycin-treated DAC paper in catch pans located under the guinea pigs and rats has greatly reduced NH_3 levels.

Future research plans include the use of an NH_3 -neutralizing substance incorporated into disposable microencapsulated absorbency pads, in place of the neomycin DAC paper. It is hoped that this procedure will give the control necessary for complete neutralization of NH_3 generated by the animals.

Ambient air is an additional source of NH_3 .⁸ This NH_3 must be removed from ambient air which supplies the chambers. The method for removal is discussed previously under chambers. This system is being modified to provide NH_3 -free air for the studies, and the preliminary results of chamber room air and chamber supply air monitoring are presented in Table II.

The room air was sampled in the vicinity of the chamber, whereas Ports 3 and 4 located on the middle tier in the Hazleton 2000 inhalation chamber (Port 3, right side, and Port 4, left side) sampled the chamber air (see Figure 1). The decrease in NH_3 levels was due to increases in the supply air relative humidity.

Future plans include using acid-soaked prefilters in the supply lines for better NH_3 removal. If needed, a scrubber may be employed (such as the one in Figure 2) to remove NH_3 to prevent the neutralization of generated acid aerosols.

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TABLE I. AMMONIA LEVELS FOR RATS VS. GUINEA PIGS

Rats (ppb)*	Rats (ppb)**	Guinea Pigs (ppb)**
227.4	81.2	54.6
210.2	77.3	30.0
295.5	48.9	62.4
236.6	66.7	37.6
278.6	40.9	58.4
249.1	22.7	56.0
415.6	34.0	79.8
259.7		56.0
Mean = 271.6	Mean = 53.1	Mean = 54.4

* Chamber air flow rate was 500 L/min (15 air changes/h) and the readings were taken over 4 h (30 rats).

** Same chamber air flow with animals using neomycin-treated DAC paper and the chamber was coated with 0.1N H₂SO₄ solution generated as an aerosol (30 rats or 30 guinea pigs).

TABLE II. AMBIENT LEVELS OF AMMONIA

Room (ppb)	Chamber Port 4 (ppb)	Chamber Port 3 (ppb)
15.0		35.4
15.4	11.2	
4.6		16.6
6.9	3.4	
4.5		19.1
4.2		6.4
4.8		7.2

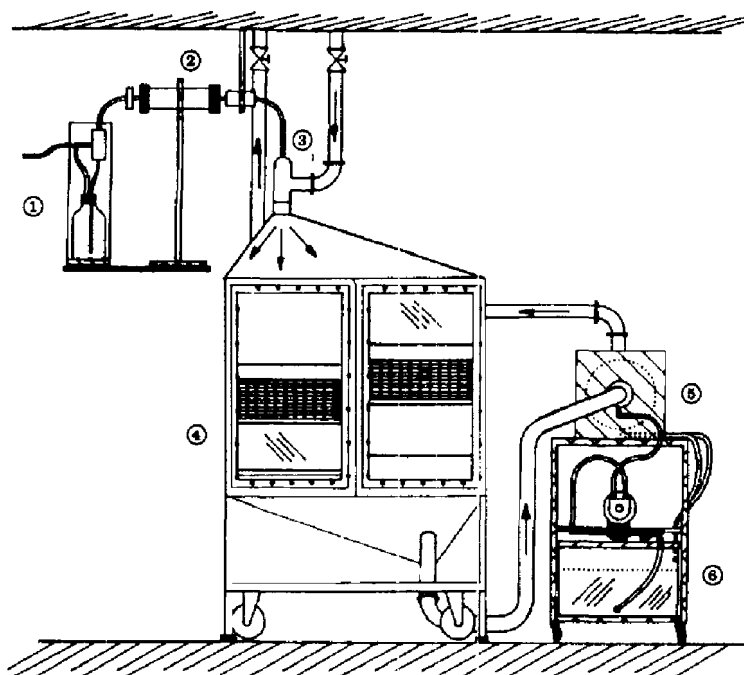


Figure 1. Acid Aerosol Exposure System – Front View. Acid aerosol will be generated from a ① pressurized nebulizer fed with acid solution by a liquid metering pump. Electrical charges on the aerosol will be neutralized by a ② ^{85}Kr source, ③ diluted, and delivered to the ④ exposure chamber. The acid aerosol is removed from the chamber exhaust by a ⑤ water scrubber. The scrubbing liquid is recirculated through a ⑥ reservoir.

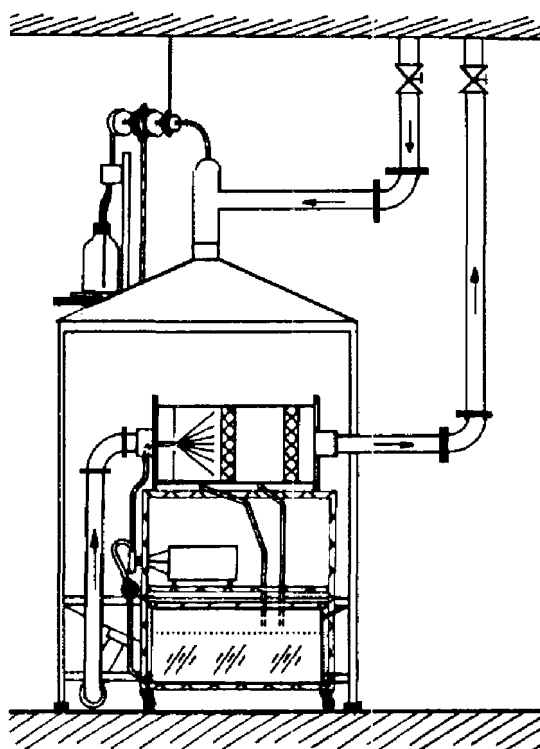


Figure 2. Acid Aerosol Exposure System – Side View.

The Atmospheric Transformation of Automobile Emissions and Measurement of the Formation of Mutagenic Products

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Automobile emissions were irradiated in a 22.7-m³ environmental chamber. The hydrocarbons for the irradiated mixture was taken from the exhaust (50%), and from a seven-component surrogate mixture (50%), representative of evaporative emissions from automobiles. NO_x came entirely from the exhaust and was brought to an initial concentration of 516 ppbv in the environmental chamber before the irradiation. The irradiation was conducted at an initial HC/NO_x ratio of 15. The mutagenic activity of the mixtures were measured using a variant of the Ames test. In this procedure, the bacteria, *Salmonella typhimurium*, strain TA100, was exposed in individual exposure chambers to the irradiated and non-irradiated effluent. The results show that the gas-phase mutagenic activity of the products is significantly greater than that of the reactants with a doubling of the irradiated mixture (over background activity) after four hours of exposure. Collection of the particulate matter from the reactant or irradiated mixtures did not yield sufficient mass to obtain either chemical or mutagenicity data above background levels. Experiments at higher concentrations were thus conducted to obtain the mutagenic activity of the particulate phase components. The measured activities of the gas phase (43 revertants/h) and the particulate phase (0.6 revertants/μg) were converted to activities per unit volume, that is, the mutagenic density which is the number of revertant/m³ of effluent. (The mutagenic density includes the potency of chemical mutagens in the mixture and the amount of these compounds present.) For the gas phase products the measured mutagenic density was 2730 revertants/m³; the mutagenic density for the particulate phase products was approximately 7 revertants/m³. The difference in mutagenic density for the two phases mostly represents the much higher mass of products present in the gas phase.

Introduction

Automobiles emit a significant fraction of the urban levels of hydrocarbons and NO_x . Automotive hydrocarbon emissions result from exhaust emissions, running losses, and other evaporative losses. In urban environments many emission sources, in addition to automobiles, contribute to the total hydrocarbon loading. On the other hand, automobiles generate a large fraction of the nitric oxide found in urban areas and on average accounts for around 60% of the urban loading for oxides of nitrogen [1]. This is due in part to the fact that most control strategies for reducing urban ozone has focused more on automotive hydrocarbon control than on NO_x control.

Several studies have been conducted to examine the effect automotive emissions have on the generation of photochemical pollutants, particularly the production of ozone. These studies have generally involved experiments performed in photochemical smog chambers, with quantitative measurements for the removal of the reactants and the generation of products. While some of the information from these studies could be used in risk assessment models, the studies are generally not designed, and are certainly not optimized, for this purpose.

In addition to ozone control, the biological effects of automobile exhaust are also of concern. Most current assessments of risk attributed to automobile exhaust are based on the composition of chemicals found in direct tailpipe emissions rather than the photochemical transformation products. However, evidence has accumulated to suggest that products generated from the photochemical transformation of the components of combusive emissions may contribute more significantly to potential health risk than do the direct emissions themselves [2].

Over the past few years research studies from several laboratories have examined mutagenic activities attributed to the photooxidation products of various atmospherically important hydrocarbons, particularly olefins and aromatics. The mutagenic activity of the gas-phase oxidation products of individual hydrocarbons (notably, propylene [3], and toluene [4,5]) have been measured and it has been determined that the gas-phase photooxidation products from these reactions can be significantly more mutagenic than are the initial reactants (i.e., notably the hydrocarbon, NO, and NO_2). In some of these studies extensive efforts have been made to identify the origin of the observed activity in terms of mutagenic contributions from individual oxidation products. While the approach has met with limited success, the results have generally indicated that a large fraction of the activity in the toluene and propylene oxidation systems is probably attributable to products (perhaps nitrogenated products) formed in low yields in the system. Experimentally measured compounds contributing to the observed activity included peroxyacetyl nitrate (PAN), the dicarbonyls-- glyoxal and methyl glyoxal, and several bifunctional organic nitrates [3].

This study has been conducted to evaluate potential mutagenicity from the components of automobile exhaust and the associated photooxidation products. The results of the study are expected to indicate the extent to which there are components in automobile exhaust which lead to the formation of mutagenic products by photooxidation processes. In addition, with current interest in alternate fuels and reformulated gasolines, the study will give baseline data from which to compare the impact these fuels and their oxidation products might have with respect to the generation of mutagenic compounds.

Experimental Methods

The main components of the apparatus include: (1) a portable dynamometer and associated dilution tunnel, (2) a photochemical reaction chamber, and (3) biological exposure chambers. Automobile exhaust was generated on-site by operating a light-duty passenger vehicle under load on a portable dynamometer. The dynamometer and accessory equipment necessary for its operation were mounted on a single flatbed trailer for turn-key operation at a remote site. A single automobile, a 1977 Ford Mustang with 40,000 miles, was employed for this study. The entire exhaust from the automobile passed through a heated, stainless-steel transfer line of 7.6-cm internal diameter which was connected to the dilution tunnel. The exhaust was diluted with ambient air that was drawn through the tunnel using a $20 \text{ m}^3/\text{min}$ turbine. Effluent from the tunnel then passed through a 7-m length of 3.2-cm Teflon tubing to reach the point where the dilute exhaust could be accurately metered into the reaction chamber.

The reaction vessel is a 22,700 L cylindrical chamber constructed of 5 mil Teflon film. The

reaction chamber is sealed to aluminum end plates that are coated with fluorocarbon paint. The radiation is generated by a combination of fluorescent sunlamps and blacklights that surround the chamber longitudinally. NO_2 photolysis rate, k_1 , as previously determined experimentally, was $0.22\text{--}0.24\text{ min}^{-1}$. Reactants introduced into the reaction chamber first passed through a 150 L inlet manifold where they were mixed with ultra-zero air. Dilution air added to the inlet manifold was supplied using a high volume clean air generator.

Four 190 L, Teflon-coated biological exposure chambers were used for the exposure of the gas-phase test mixtures to the biological assay. The activity of irradiated gas-phase effluent was measured in an exposure chamber situated in close proximity to the reaction chamber to minimize transfer losses for reaction products of low volatility. The gas-phase mixture entering this exposure chamber was filtered with a 135 mm Teflon-impregnated glass fiber filter. The exhaust from this chamber was then fed into a second exposure chamber in series. This chamber, the carry-over chamber, was employed to determine the extent to which mutagenic compounds pass through the initial exposure chamber. Also included were chambers to measure the activity of the reactants and the background activity of clean air. All exposure chambers were operated at a flow of 14 L/min.

The bacteria *Salmonella typhimurium*, strains TA100 and TA98 were employed as the biological assay for this study. 45 ml of base agar (Difco) was poured into glass petri dishes. The plates were seeded with bacteria using 0.1 ml of the *S. typhimurium* culture containing 1×10^8 bacteria mixed in a 3 ml of an agar overlay. The overlay was poured at a temperature of 45°C . In formulating these plates minimal histidine at the same final concentration as prescribed was placed in the base agar rather than in the top agar. Since only direct activity was determined in these experiments, metabolic activating substances such as S9 were not added to the active mixture. Colony counting of the expressed bacteria was performed using a Biotran III automatic colony counter. All other procedures using the biological assay followed those previously described [6].

The reacting hydrocarbons for this study derived from two sources, the automobile exhaust and a hydrocarbon surrogate mixture. The gasoline used to power the automobile in this study was a commercially available winter-grade unleaded fuel. The surrogate component was derived from a seven-component chemical mixture representative of vehicular evaporative losses.

The experimental procedures generally followed those previously described for gas phase exposures of both simple hydrocarbons, as well as those for other complex mixtures. The procedures for these experiments were refined to address the constraints of this combustion source with respect to viable operation of the reaction chamber. Automobile exhaust and the surrogate hydrocarbon mixture were admitted into the chamber using the following procedure. The automobile was operated using a 23 minute driving cycle followed by a ten minute idle. The automobile exhaust from the dilution tunnel, was mixed with zero air in the inlet manifold and injected into the reaction chamber at the requisite flow. The integrated HC/NO_x ratio of the automobile exhaust over the complete 33 minute cycle was between 7 and 8. The exhaust was metered into the inlet manifold at a rate necessary to yield an integrated NO_x chamber concentration of approximately 500 ppbv. The total hydrocarbon contribution from the exhaust amounted to 3.75 ppmC, approximately 40% of which was generated during the driving cycle and 60% during the automobile's idling period. The remaining 3.75 ppmC was provided from the evaporative surrogate mixture by bubbling nitrogen at a flow of about 0.5 ml/min through the liquid surrogate mixture and feeding the headspace vapor simultaneously with the exhaust into the inlet manifold.

The irradiation was conducted by bringing the reaction chamber up to the desired reactant concentrations with automobile exhaust and the surrogate mixture. The irradiation began by operating the chamber in a static mode to reach the desired extent of reaction. The initial mixture was irradiated until the ozone maximum was attained which required six to eight hours. When the ozone maximum concentration was reached, the operation mode for reaction chamber was changed from static to dynamic mode. This change required a short transition period (ca. 2 h.) for the effluent to reequilibrate to the exact conditions of the experiment. Following the transition period the biological exposure chambers were filled with approximately 25 plates each of TA100 and TA98. Also included were survivor plates for each exposure condition. These plates served as an initial screen to evaluate the degree to which the biological assay might experience toxicity from the test mixtures. The exposure chambers were flushed with the appropriate effluent until the concentrations in the exposure chambers reached a steady state value. The petri dish covers were then removed beginning the exposure. Predesignated groups of test and survivor plates were covered during the course of the exposure to generate a dose-response relationship. For

statistical purposes, 7-8 plates were employed for a single exposure. Before and during the exposure, chemical analyses of the components in the reaction chamber, exposure chambers, and mixing manifold were obtained at regular intervals.

Results and Discussion

Initial conditions for the photooxidation experiment are shown in Table I. An initial NO_x concentration of 516 ppbv was used. This concentration lies at the upper end of ambient NO_x concentrations which have been measured [7]. NO_x generated in automobile combustion is largely composed of NO and in this experiment NO comprised 88% of the total NO_x initially present. The values for NO and NO_x were determined from a weighted contribution of the reactant material present at the start of the static irradiation and that added during dynamic mode operation. Although the concentrations of added exhaust components were not constant with time, the car was operated on a driving cycle giving a cyclic and reproducible input of reactants.

Table I also gives product information for the experiment before and following irradiation. The residence time of the mixture in the reaction chamber was 6.3 hours. The dominant products detected other than ozone were aldehydes and to a lesser extent peroxyacyl nitrates for which aldehydes are often the dominant precursors. Formaldehyde and acetaldehyde increased by at least an order of magnitude by the time steady-state was reached. Most of the other carbonyl and dicarbonyl compounds increased from below the detection limit to concentrations between 5 and 50 ppbv. PAN was present at a concentration of 88 ppbv. Peroxypropionyl nitrate (PPN) and peroxybutyryl nitrate (PBN) were also detected on the same chromatogram as was PAN. Although standards were not available for the calibration of PPN and PBN, their concentrations based on the instrumental sensitivity for PAN could be estimated. PPN amounted to approximately 9% of the PAN concentration and PBN to approximately 6%.

The activity measured in TA100 for the reactant and product mixture is shown in Figure 1. The mutagenic activity of the reactants (dotted line) showed an activity of 8 revertants/h, although this activity was not reproducible in other measurements of the reactant mixture. The exposure of the photooxidation products to TA100 gave a substantial increase in the mutagenic activity above that of the reactants. As given in Figure 1, the slope of the dose-response curve (solid line) produced an activity of 43 revertants/h. The dashed line in Figure 1 represents the activity of the carry-over component of the effluent and gave a value of 21 revertants/h.

The mutagenic activity of the gas phase can also be placed on an air volume basis, that is, the number of revertants generated from gas-phase mutagenic species per m^3 of effluent. The calculation is made using the following relationship [8],

$$M_{\text{gas}} (\text{rev}/\text{m}^3) = m_{\text{gas}} (\text{rev}/\text{plate-h}) \times N (\text{plates}) / V_{\text{gas}} (\text{m}^3/\text{h}) \quad (1)$$

where M_{gas} is the mutagenic density of the gas phase, m_{gas} is the mutagenic activity of the gas phase as given above, N is the total number of plates in the exposure chamber, and V_{gas} is the volume of effluent passing through the chamber per hour of exposure. For the reactants with an activity of 8 rev/plate-h the calculated mutagenic density is 510 revertants/ m^3 . For the effluent with an activity of 43 rev/plate-h, an activity of 2730 revertants/ m^3 is determined.

The number and volume distributions for the particulate matter were measured before the irradiation and at the maximum in the ozone concentration. Before irradiation, the integrated number distribution (between 0.01 and 1 μm) was 1.3×10^3 particles/cc. This value rose following irradiation to 1.1×10^4 particles/cc and suggested the occurrence of secondary particle formation [4]. The total volume of the particles between 0.01 and 1 μm increased by a factor of five following irradiation from 0.7 nl/m^3 to 3.6 nl/m^3 .

Particulate matter from the products collected on filters during the exposures was insufficient to obtain reliable identifications of individual chemical components by GC/MS. (The particulate concentrations of the reactant mixtures were already extremely low.) This was indicated by filter weights and the total volume measurements of the EAA which is related to the total mass between 0.01 and 1.0 μm . An analogous problem was encountered for the biological analysis. Given the low absolute amount

of sample collected and the statistical uncertainties using the Ames assay, the measured revertant levels were not statistically different from the background revertant levels. This occurred for both the reactants and effluent. However, an experiment was conducted using reactant concentrations an order of magnitude higher than that of the previous experiments. In this experiment the initial total hydrocarbon value was 80 ppmC and the initial NO_x value was 5 ppmv. Photooxidation of this mixture yielded values for the mutagenic activity of the reactants (1.1 rev/μg) and products (0.6 rev/μg). Given the approximate particulate concentrations in the effluent of 2 μg/m³ for the reactants and 11 μg/m³ for the products, this lead to mutagenic densities for the particulate phase of 2.2 rev/m³ for the reactants and 6.6 rev/m³ for the product mixture.

Thus, for the reactants and products in this experiment, the mutagenic density of the gas-phase components outweigh the contributions of the particulate-phase components. However, it must be recognized that this report represents a single experiment employing a single vehicle, using a single fuel and operated under a single driving cycle; any generalizations from the results of this study must take this into account and may not be applicable to different conditions.

Disclaimer

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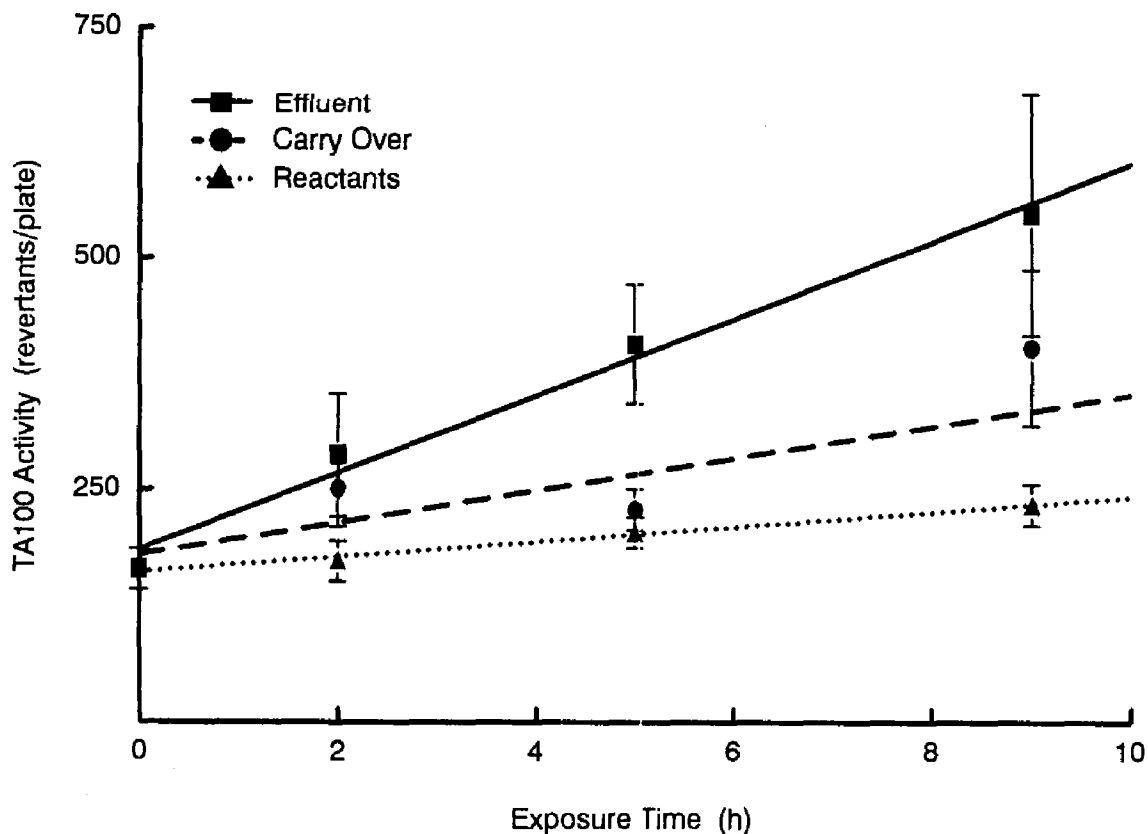
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Table I. Concentrations of measured reactant and product species from the photooxidation of automobile exhaust and evaporative surrogate mixture.

Species (initial)	Conc (ppbv)	Species (final)	Conc (ppbv)	Species (final)	Conc (ppbv)
NO	454	NO	0	CH ₃ C(O)CH ₃	54
NO _x	516	NO _x	375	MEK	25
THC,ppmC	7.9	THC,ppmC	5.7	C ₃ H ₇ CHO	11
HCHO	16	HCHO	176	C ₄ H ₉ CHO	8
CH ₃ CHO	3.6	CH ₃ CHO	89	C ₆ H ₅ CHO	2
		O ₃	516	CHOCHO	11
HC/NO _x	15.3	PAN	88	CH ₃ CHO	7

Figure 1. TA100 activity from automobile emissions and their irradiated products



VALIDATION OF METHODOLOGY FOR DIRECT BIOASSAY
OF ATMOSPHERIC VOLATILE ORGANIC COMPOUNDS

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The Ames/Salmonella assay has been used to detect mutagenicity of organic extracts of ambient air particulate and this mutagenicity has been correlated with industrial activity. Little is known about the potential mutagenicity of volatile organic compounds (VOCs) because adequate bioassay techniques have not been available. A need therefore exists to directly assess the mutagenic activity of ambient air VOCs. Studies were conducted to validate methodology developed for the bioassay of ambient air VOCs as collected via Tenax cartridges.

Tenax-based collection and chemical analysis of VOCs are well-established methods, and were used, with modifications, for this work. A large glass cartridge containing 12 g of Tenax was used in order to sample sufficient quantities of air for bioassay detection of ambient levels of most VOCs. A technique for measuring the mutagenic activity of volatile compounds was recently developed, and was validated with known quantities of specific target compounds. The two procedures, i.e. Tenax collection and VOC bioassay, were combined as a single technique that will permit direct assessment of the mutagenic potential of atmospheric samples. Four representative VOCs (halogenated and epoxy organics) were individually spiked into large cartridges and desorbed into the Tedlar bag bioassay system. Response curves were obtained for duplicate experiments for each compound. The results showed good correlation between spiked quantities and mutagenic response; acceptable precision was demonstrated for each VOC. Dose ranges for each VOC were at levels of several hundred micrograms, which can be accommodated by the cartridges used for this study.

Introduction

Background

The Ames Salmonella assay has been shown to detect animal genotoxic substances as mutagens in a cost- and time-efficient manner^{1,2}. The assay has been utilized to detect mutagenicity of organics from ambient air particulate and the mutagenicity has been correlated with industrial activity³. The literature contains many references on the use of the Ames assay for similar studies, but little is known about the potential mutagenicity of volatile organic compounds (VOCs) because adequate bioassay techniques have not been available. The volatile component of ambient air pollutants represents a potentially greater human health risk than condensed phase materials since their atmospheric load is more than an order of magnitude greater⁴. Thus a means of collecting and testing VOCs using the same general Ames system that is used for other pollutant mixtures would provide a useful tool for assessing total mutagenicity/carcinogenicity of collected air samples.

The interface of volatile (boiling point < ~ 130°C) and, in many cases, lipophilic compounds with an aqueous based assay conducted at elevated temperatures presents many problems. These problems were largely circumvented following research efforts at the RTI and EPA laboratories some years ago⁵. An assay method was developed that utilized a closed system (Figure 1) wherein vapor phase substances were equilibrated and incubated with standard pour plates. The method uses a small Tedlar bag (~ 500 mL) fitted with a septum-containing inlet, and containing one (or more) standard pour plate.

To serve as a practical means of assessing mutagenicity of ambient air levels of VOCs, it is necessary to effect an interface with a VOC collection method. One of the most effective of the many existing methods is the use of Tenax polymeric sorbent for entrapment of VOCs from air. This methodology was developed at RTI, and is well validated, having been used for the collection and analysis of several tens of thousands of samples. An obvious choice then for the overall methodology of collecting and determining the mutagenic potential of ambient air VOCs involved a combination of Tenax based sampling and Tedlar bag bioassay. The validation of the combined techniques is the subject of this manuscript.

Experimental Approach

The general scheme for method validation involved loading Tenax cartridges with known amounts of representative VOCs, and thermally desorbing the VOCs into a Tedlar bag bioassay system. Mutagenic response was assessed by recording the number of revertants at several dose levels, and comparing these data with experiments involving direct injection of known quantities of VOCs into the Tedlar bags. The study was limited to VOCs that were known to yield linear responses in doses ranging from several hundred to over 1000 µg. These ranges were required by the sensitivity of the bioassay test system, which then also dictated the amount of Tenax needed for the study. To trap hundreds of micrograms of airborne VOCs requires the use of a large cartridge with a capacity of more than 10 g of Tenax. Optimization studies were conducted to establish effective trapping/desorbing/analysis conditions for the large cartridge system.

Replicate experiments were conducted with each of four VOCs. Compounds studied to date include epichlorohydrin (EPC), ethylene dibromide (EDB),

propylene oxide (PO) and butylene oxide (BO). Recovery studies were carried out for two of these analytes. Precision and recovery data, and results from the comparison of the Tenax-introduced versus the direct injection methods, provided the requisite procedure validation.

Experimental Methods

Tenax Methodology

The general methodology for Tenax sampling and analysis of ambient air has been described elsewhere, most recently by Pellizzari et al.⁶ All work detailed in this report for Tenax preparation, loading and desorption followed the published methods. Minor modifications were incorporated into the method because of the use of a larger cartridge, and to allow direct injection of desorbed VOC into a Tedlar bag. A schematic of the desorption system is shown in Figure 1. Glass cartridges were fabricated to contain ~12 g of Tenax (35-60 mesh). Cartridges were 3 cm wide, 21 cm long, and contained tapered ends (to 1.5 cm width) to accommodate existing connectors that are used routinely for analytical Tenax cartridge work. A thermal desorption unit was also fabricated to contain the larger cartridge; this unit is identical, with the exception of scale, to analytical cartridge units. A small bore access port was fashioned into the desorption chamber cap to allow direct injection (syringe) of test compounds for recovery studies. For introduction of desorbed/cryotrapped compounds into the Tedlar bag system, a short section of heated SS tubing (~ 150 x 1 mm OD) was led from the valve (Figure 1) and coupled with a 5 cm section of Teflon tubing. A SS needle (21 gauge) was inserted in the end of the Teflon tubing for injection of the VOC into the Tedlar bag. For desorption studies, ethanolic solutions of test compounds were spiked onto Tenax cartridges via a flash evaporation system. Routinely, 1-3 μL of solution were used for preparing all dose levels.

Bioassay Method

The methodology utilized for all Tedlar bag bioassay work has been described⁵. In order to maintain the integrity of the closed test system (Figure 2), each bag was sealed with tape, then leak-checked with a leak detector. Each bag, prior to the introduction of Tenax-desorbed compound, was physically compressed to remove as much internal air as possible. This allowed for the ready accommodation of 250-350 mL of vapors from the desorption system. For this study, only a single tester strain of bacteria (TA100) was used, without S9 activation. Positive controls consisted of propylene oxide (500 μg), 2-anthramine (2.5 μg) and sodium azide (2.5 μg). Blanks consisted of bacteria with and without ethanol. Bags were incubated for 48-56 hours in a 37°C incubator. Colonies were counted with an automatic colony counter.

Results

Optimization/Recovery Studies

The general conditions for trapping and desorbing the smaller, analytical-scale Tenax cartridges were used as a starting point for establishing similar conditions for the large cartridges. Although a trap constructed from capillary tubing is used for analytical work, the larger quantities of desorbed components for this study led to the use of a large bore (2.1 mm ID) stainless steel trap. Several experiments were conducted to determine the optimum trap configuration. All such work utilized liquid nitrogen as

a coolant for the trap. Based on previous work conducted at RTI and by others, glass beads were also used in the optimization studies. The trap geometry finally adopted for all validation work included a "U" shaped section of tubing, 30 cm in length, containing a 10 cm bed of glass beads (200 mesh). Although initial work utilized a boiling water bath for desorption of trap contents, a higher temperature was shown to be more effective. Final overall trapping/desorption conditions are shown in Table I; also included in the table are the GC conditions used in the recovery studies.

Recovery data was generated for the first two compounds studied, epichlorohydrin (EPC) and ethylene dibromide (EDB). Desorbed compounds were diverted to a capillary GC system (Table I) for flame ionization detection and data acquisition. All recovery experiments were conducted by comparison of area counts for peaks associated with desorbed material from spiked cartridges, with area counts from similar quantities of material injected directly into the desorption chamber. For EPC, an initial experiment was conducted at a single dose level (500 μ g); for EDB, recoveries at three dose levels were determined. Experiments were conducted in triplicate or quadruplicate for the test compounds. Given the excellent precision associated with direct injection for the EPC work, only single injections were made for the EDB study. As shown, the recoveries were high (average ~ 83 %) and were virtually independent of compound type or dose level.

Bioassay Studies

Mutagenicity results for each of the four compounds studied are shown in summary form (Table III) and as plots (Figures 3 and 4) of response versus dose. Each plot contains data for results from directly injected and Tenax-introduced test compound. Dosing levels, response ranges, and pertinent statistical data are shown in Table III for all four compounds. Each figure shows two plots corresponding to each of two separate experiments. In general, linearity of response was quite good, although in some instances, e.g. EDB and BO, deviation from linearity at higher dose levels was evident. The mean correlation coefficient for all sixteen experiments was approximately 0.93, while overall precision (mean of %RSD for all data points for all sixteen runs) was less than 12 %RSD. In all cases, mutagenicity for Tenax-introduced assays were less than for direct injection assays. This is presumably due to simple differences in recovery for the two modes of introduction of test compound. The data reflect very adequate responses and show acceptable levels of linearity and precision.

Conclusions

The procedure for introduction of VOCs into a previously validated closed mutagenicity bioassay system using Tenax desorption techniques has been shown to be effective, precise and reliable for recovery and detection of mutagenic VOCs. The successful results obtained for four mutagenic and volatile test compounds serves to validate the desorption/bag interface, and thus represents a possible method for the direct assessment of mutagenic potential of ambient or other types of atmospheric samples. Field validation experiments using the combined techniques are in progress.

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Table I. Final system operating conditions.

Desorption Parameters	GC Conditions
Purge Gas Flow Rate: 50 mL/min	Column Type: Fused Silica, SE-54 (30 m x 0.32 mm ID)
Desorption Chamber Temperature: 270 °C	Column Temp (background check): 45 °C (5 min), 45 - 160 °C @ 40/min, 160 °C (5 min)
Desorption Time: 15 min	Column Temp (compound analysis): 45 °C
Trap Temperature (collection): -196 °C	Carrier Gas Flow Rate: 0.96 mL/min
Trap Temperature (purge): 200 °C	Injector Temp: 160 °C
Purge Time: 5 min	Detector: FID
Trap Design: ss "U" tube, 300 x 2.1 mm ID, with 10 cm bed of glass beads, 200 mesh	Detector Temp: 300 °C
	Split Ratio: 47:1

Table II. Recovery data.

Compound (Amount)	Peak Area Counts (x10 ⁴)		Recovery (%)
	Cartridge	Direct Injection	
Epichlorohydrin (500 µg)	604.6	730.6	78.8
	522.8	741.1	
	<u>612.0</u>	<u>734.4</u>	
	579.8 (8.5% RSD)	735.4 (0.7% RSD)	
Ethylene Dibromide (600 µg)	201.0	227.4	86.2
	208.9		
	183.7		
	<u>190.2</u>		
Ethylene Dibromide (840 µg)	196.0 (5.7% RSD)	326.7	83.7
	285.6		
	276.7		
	251.1		
Ethylene Dibromide (1080 µg)	<u>280.0</u>	417.6	82.5
	273.4 (5.6% RSD)		
	368.5		
	342.8		
	336.0		
	<u>330.4</u>		
	344.4 (4.9% RSD)		

Table III. Bioassay test data.

Compound	Dose Range (μg)	Response Range (rev.)	Linearity ^a	Precision ^b
EPC	100 - 600	~500 - 1400	0.933	~11% RSD (Dir. Inj.) ~13% RSD (Tenax)
EDB	500 - 1080	~300 - 700	0.877	~7% RSD (Dir. Inj.) ~12% RSD (Tenax)
PO	400 - 960	~500 - 1100	0.944	~11% RSD (Dir. Inj.) ~9% RSD (Tenax)
BO	600 - 1200	~400 - 800	0.963	~5% RSD (Dir. Inj.) ~15% RSD (Tenax)

^aAverage correlation coefficient from least squares regression for all 4 runs.

^bAverage of all response values for the two Dir. Inj. experiments and the two Tenax experiments.

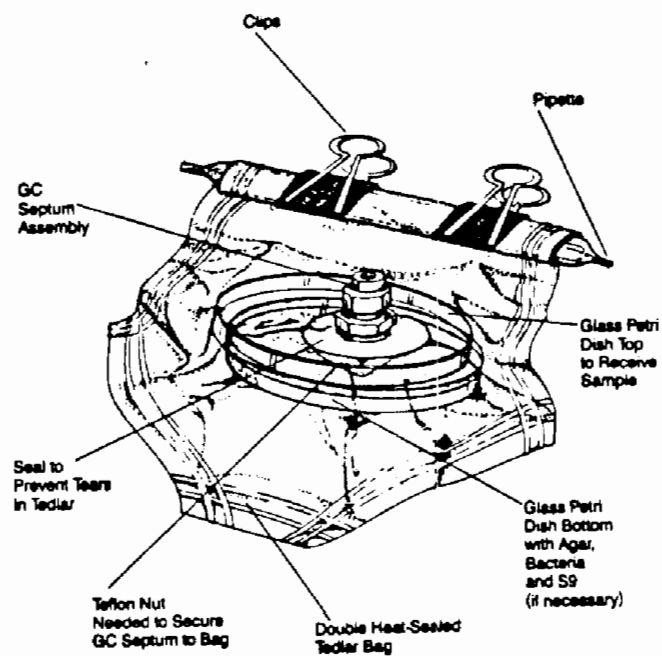


Figure 1. Closed bioassay system for organic volatiles.

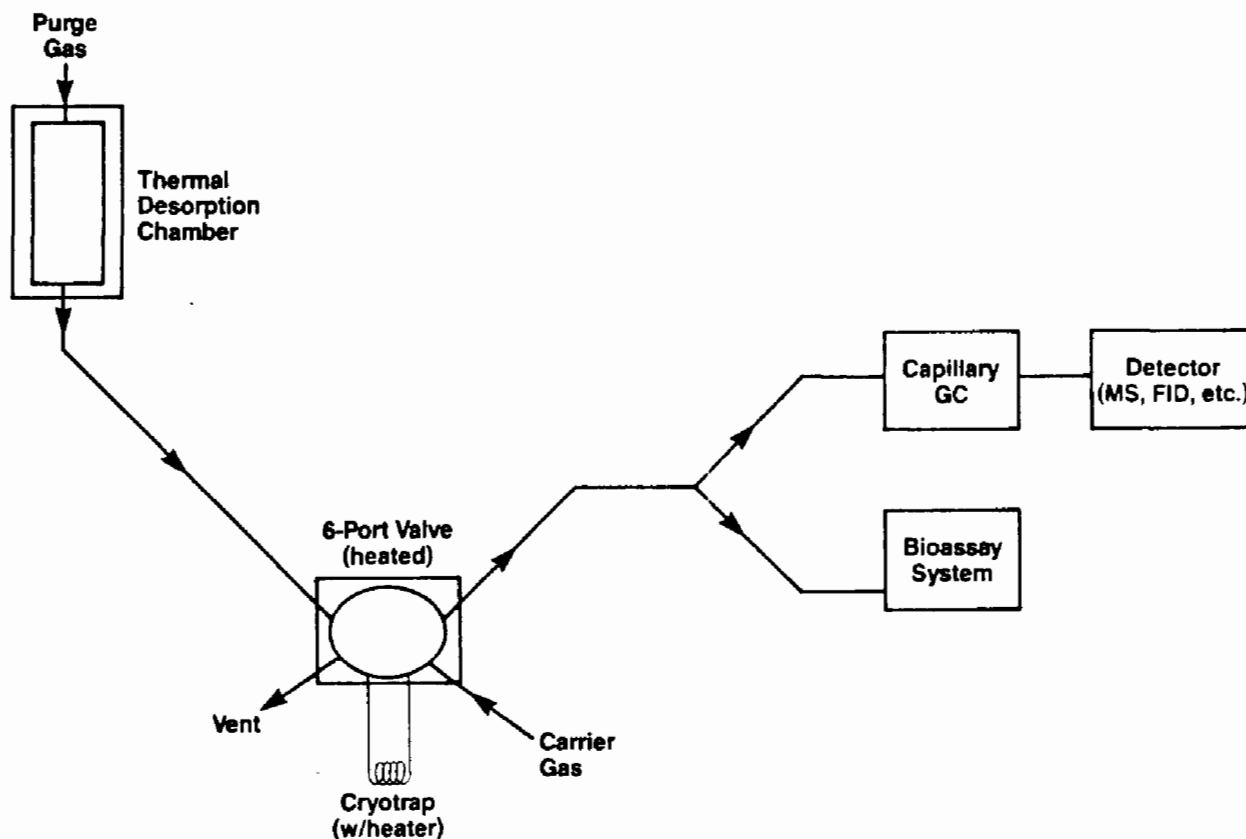


Figure 2. Schematic of Tenax desorption system.

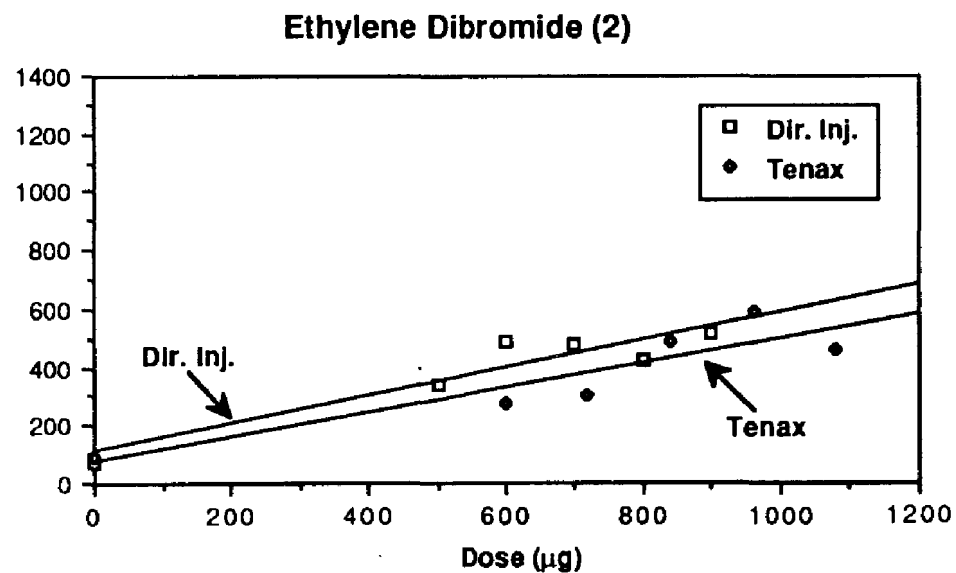
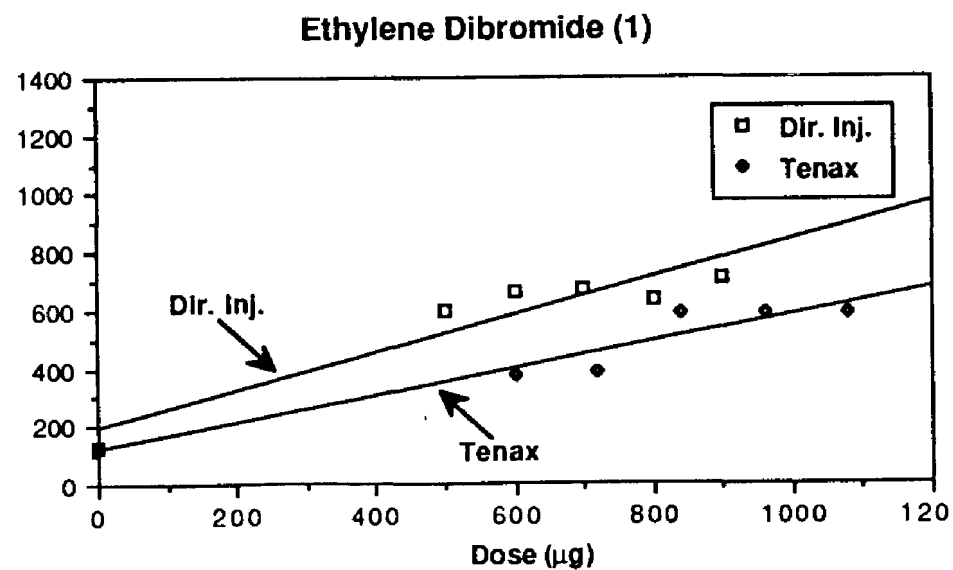
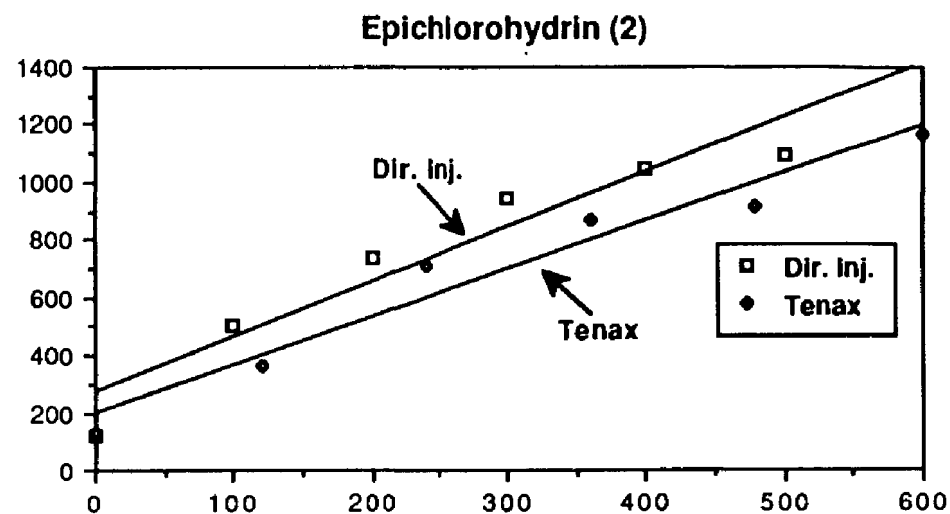
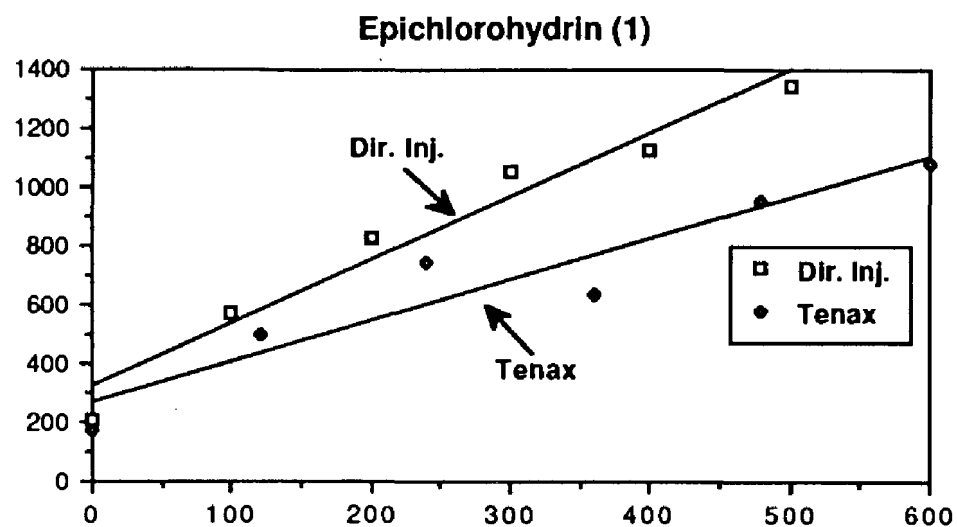
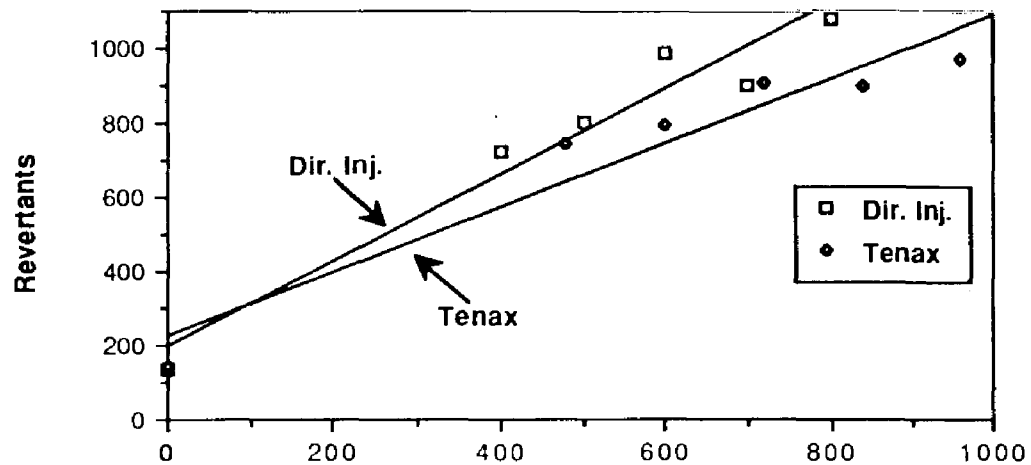
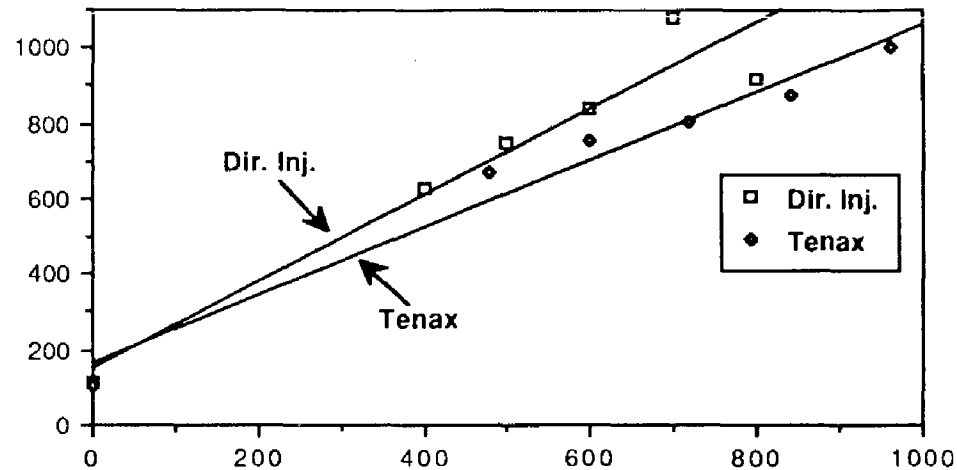


Figure 3. Bioassay results - duplicate experiments.

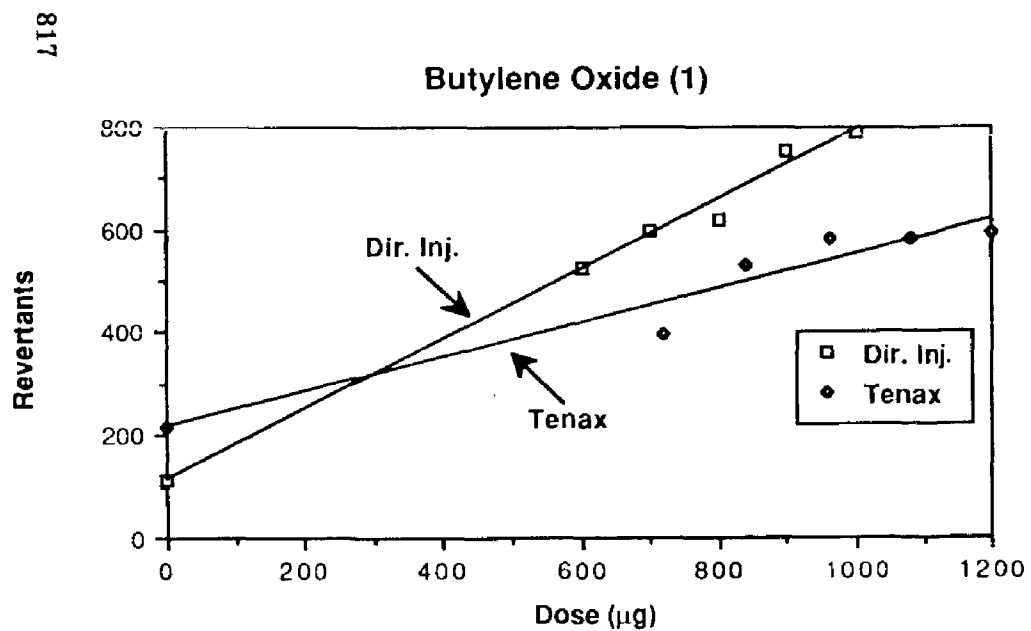
Propylene Oxide (1)



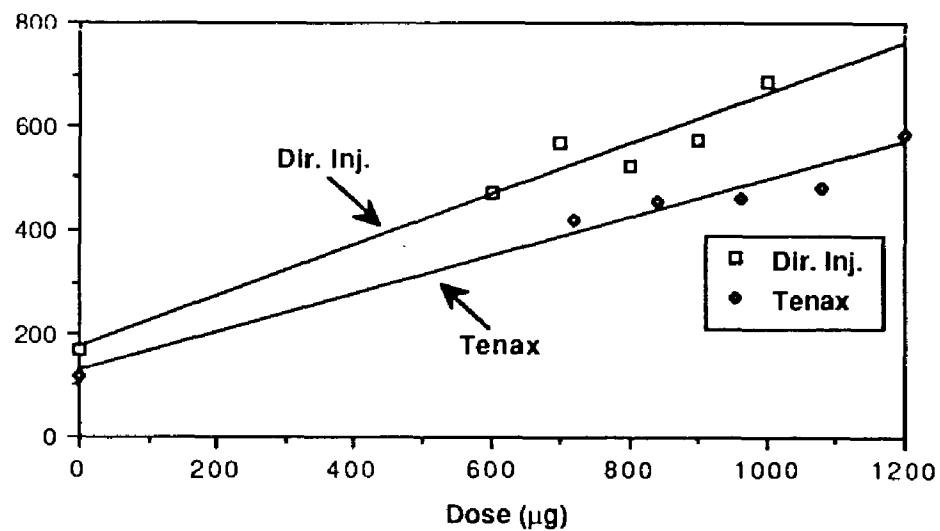
Propylene Oxide (2)



Butylene Oxide (1)



Butylene Oxide (2)



ISOLATION OF MUTAGENS IN AMBIENT AIR PARTICULATE EXTRACTS USING BIOASSAY-DIRECTED FRACTIONATION

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The bioassay-directed fractionation of mutagens in Boise, ID ambient air particulate extracts was initiated using two levels of fractionation. First, two composite samples, a wood smoke composite (WSC) and a mobile source composite (MSC), were fractionated using nonaqueous anion solid phase extraction (anion-SPE). In five runs, recoveries of mass and mutagenicity from both samples were consistently good with ca. 85% to 95% of the mass and ca. 85% to 100% of the mutagenicity being recovered. A standard mixture containing basic, neutral and acidic compounds was also fractionated to verify acid/neutral-base separation. The anion-SPE strong acid fraction was chosen for further component separation using normal phase cyanopropyl HPLC (CN-HPLC). In the second level fractionation, quantitative recoveries of both mass and mutagenicities were recorded. The preliminary data describing the distribution of mass and mutagenicity between fractions in both levels of fractionation are described.

Introduction

Isolation and identification of potential cancer causing compounds from the innumerable components of ambient air complex mixtures is, at best, a formidable task. However, by using the process of bioassay-directed fractionation, mutagens may be isolated from the non-mutagens by developing methods that target those sample fractions that exhibit the greatest mutagenicity.¹ The general approach is to initiate a multi-level fractionation based upon the broad chemical properties of the sample components. In each successive level, the most mutagenically potent fractions are chosen for additional, more selective fractionation. The principal goals for all developed methods are quantitative mass and mutagenicity recoveries, isolation of mutagen enriched fractions, and the subsequent identification of the mutagenic compounds.

We initiated our fractionation scheme in two distinct fractionation levels that separate sample components based on ionic character and

polarity (Figure 1). For the first level we developed a method similar to that reported by Bell et al.² for isolating acidic sample components from neutral and basic components. For the second level, we developed a fractionation procedure that separated the sample into nonpolar, moderately polar and polar fractions. Reported here are the preliminary data on the fractionation of two ambient air particulate extract composite samples and a standard mixture.

Experimental

Reagents

All solvents, methanol (MeOH), dichloromethane (DCM) and hexane, were obtained from Burdick and Jackson (Muskegon, MI). The anion exchange resin, AG MP-1, was obtained from Bio-Rad (Richmond, CA). The trifluoroacetic acid (TFA) was obtained from Aldrich (Milwaukee, WI) and the CO₂ was obtained from National Specialty Gases (Raleigh, NC).

Samples

Standard mixture. The standard mixture (STD), in DCM, was composed of pyrene (1.81 mg/mL), 1-naphthol (1.47 mg/mL), benzoic acid (0.57 mg/mL), 7,8-benzoquinoline (1.46 mg/mL), 2-nitrobenzoic acid (1.57 mg/mL), and 4-nitrophenol (1.37 mg/mL), all obtained from Aldrich (Milwaukee, WI). The mixture also contained 1-nitronaphthalene (1.61 mg/mL) from Chem Service (West Chester, PA).

Composite Samples.³ The composite samples were prepared from the extractable organic matter (EOM) of 100 Boise, ID, Elm Grove Park (EGP) and Fire Station samples (50 each divided between daytime and nighttime). A single element tracer multi-linear regression (MLR) model was applied to the EOM mass of each sample using soil corrected fine particle potassium and fine particle bromine as tracers for wood combustion and mobile sources, respectively. Samples showing the greatest wood smoke impact were combined until a total of ca. 2.5 grams had been gathered to form the wood smoke composite (WSC) sample. The mobile source composite (MSC) sample was prepared in the same manner using samples more heavily impacted with mobile source combustion. Based upon trace modeling, the percent wood smoke contribution to the final two composite samples were ca. 89% for the WSC and ca. 64% for the MSC.

Level 1: Nonaqueous Anion Solid Phase Extraction (Anion-SPE)

Resin Preparation. The AG MP-1 resin (100 - 200 mesh) was prepared for use by washing 200-300 mL resin with 300 mL 1% TFA/MeOH for 10 min, then 500 mL MeOH for 10 min, followed by 500 mL 0.10 M KOH/MeOH solution for 10 min, then another 10 min MeOH wash and finally rinsed with copious amounts of deionized water. The resin was then Soxhlet extracted sequentially in 500 mL MeOH for 16 hours, 850 mL DCM for 24 hours and finally 850 mL MeOH for 24 hours. A portion of the clean resin (15 mL) was then placed into a 30 cc syringe plugged with silane treated glass wool. The syringes were then placed onto a Baker solid-phase extraction vacuum manifold (SPE 10 system).

Fractionation Procedure. Samples, ca. 20 to 30 mg in DCM, were concentrated and placed directly onto the resin in 250 μ L aliquots per column. The five collected fractions were each eluted with 24 mL aliquots of the respective solvent. The elution order was DCM, MeOH, CO₂/MeOH (prepared by bubbling CO₂ in methanol for 30 min), 2% TFA/MeOH and for runs

3 through 5 an additional 10% TFA/MeOH fraction was eluted. The DCM, MeOH and CO₂/MeOH fractions were rota-evaporated to ca. 2 mL. To ensure adequate removal of the TFA, we took advantage of the TFA/MeOH azeotrope; the 2% and 10% TFA/MeOH fractions were diluted to ca. 50 mL with MeOH, rota-evaporated to ca. 5 mL, rediluted to ca. 50 mL and concentrated to a final volume of ca. 2 mL. Finally, all samples were quantitatively transferred to a 10 mL volumetric flask and diluted to volume with DCM.

Reversed Phase HPLC. The HPLC experiments were performed with a Hewlett Packard Model 1090 instrument in conjunction with a Valco Instruments six-port HPLC valve and a Waters Model 440 UV detector (254 nm). A Du Pont (Wilmington, DE) Zorbax ODS reversed-phase HPLC column (0.46 x 25 cm; 10 μ m particles) was used. The distribution of the standard mixture components between the fractions was determined using a linear gradient of 50% to 100% MeOH/H₂O in 10 min at 2.0 mL/min.

Microbial Mutagenicity Methods. The collected fractions were assayed for mutagenicity toward Salmonella typhimurium strain TA98 with and without exogenous metabolic activation (+ or - S9, respectively) using the Ames plate incorporation assay.⁴ The fractions were tested with duplicate plates at four to five dose levels (5 ug - 200 ug), depending on the availability of sample mass. Mutagenic potency was defined as the slope of the dose-response data, calculated by simple linear regression on the first four dose levels for each sample.

Level 2: Cyanopropyl HPLC (CN-HPLC)

CN-HPLC. The HPLC experiments were performed with a Varian Model 5000 instrument in conjunction with a Valco Instruments six-port HPLC valve and a ISCO Model 1840 UV detector. A Keystone Scientific (State College, PA) Deltabond cyanopropyl (CN) HPLC column (0.46 x 25 cm; 5 μ m particles) was used. The CN-HPLC fractionations of the strong acids from the anion-SPE experiments were performed in three 25 min steps of 100% hexane, 100% DCM and 100% MeOH, respectively at 2.0 mL/min. Three minute gradients were used to progress from one step to the next. The collected fractions were then concentrated to a final volume of 1.0 mL.

Results

Level 1: Nonaqueous Anion Solid Phase Extraction (Anion-SPE)

To characterize the nonaqueous anion-SPE method, five fractionations of each sample (WSC, MSC, and STD) were performed with corresponding blank runs. The mutagenicity and mass recoveries were calculated for each run and averaged for each sample (Table I). The anion-SPE fractions of the standard mixture were analyzed by reversed phase HPLC and the percent distribution of the individual standards between fractions determined (Table II). As shown in Figure 2, both the DCM and TFA fractions demonstrated the greatest mutagenic potencies. Although both samples would eventually be used in the second level fractionation, we chose the TFA/MeOH fractions for the continuation of this study.

Level 2: Normal Phase Cyanopropyl HPLC

Two TFA/MeOH samples were used in the second level normal phase HPLC. Sample #1 was prepared from the TFA/MeOH fractions of two anion-SPE runs that were performed on old AG MP-1 which caused slightly anomalous results; most of the mass in the TFA/MeOH fractions eluted in the 2% TFA/MeOH fraction rather than an even distribution between the 10% and 2% TFA/MeOH

fractions. Although the exact nature of sample #1 was somewhat ambiguous, the sample proved useful in the initial stages of level 2 methods development. Sample #2 was composed of the residual mass in the TFA/MeOH fractions of three anion-SPE runs discussed above. To characterize the CN-HPLC method, three runs were made using sample #1 (ca. 0.70 mg, 1.23 mg, and 2.23 mg injections) and two runs made using sample #2 (ca. 870 μ g injections). The mass and mutagenicity recoveries are reported in Table III. A comparison of the percent mass distribution between fractions of sample #1 and #2 (all runs) are shown in Figure 3 along with the mutagenic potencies of each fraction.

Conclusion

Although the data presented here is preliminary, the results are very promising. We have achieved consistently high recoveries of both mass and mutagenicity. In addition, the level 2 HPLC experiments have yielded a nonpolar acid fraction which contains ca. 45% of the sample mutagenicity while containing only ca. 20% of the total sample mass. This novel, mutagenically potent fraction is in the process of being analyzed using GC/MS in hopes of identifying some of the components. Because of the limited mass available for GC/MS analysis, we have only been able to tentatively identify what appears to be a hydroxylated nitro compound. We are also in the process of characterizing a new anion-SPE protocol which differs from the original procedure in three principal ways. We are now using only 1.5 mg of resin for the same sample mass and collecting the strong acids in only one 15 mL fraction of 10% TFA. In addition, we are testing the use of the AG MP-1 resin without the extensive soxhlet extraction pretreatment.

Acknowledgements

We thank Gwendolyn Belk, Virginia Houk and Maria Taylor for their invaluable assistance in this research. We also thank Roy B. Zweidinger and Joellen Lewtas of the U.S. EPA and William Ellenson of NSI-ES for their critical comments and helpful suggestions throughout this project. We also thank the U.S. EPA Integrated Air Cancer Project for funding this research through contracts #68-02-4443 to NSI and #68-02-4456 to EHRT.

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Table I. Level 1: anion-SPE average mass and mutagenicity recovery.

Sample	Mass	Mutagenicity	
	PERCENT Recovery	Recovery (+/-) S9	Reconstituted (+/-) S9
MSC	91%	95%/102%	151%/131%
(RSD)	(.05)	(.14/.10)	(.12/.17)
WSC	83%	85%/88%	117%/112%
(RSD)	(.06)	(.1/.08)	(.10/.14)
STD	99%	-	-
(RSD)	(.22)	-	-

Table III. Level 2: CN-HPLC recovery of mass and mutagenicity.

SAMPLE 1		
RUN #	MASS Recovery	Mutagenicity Recovery
1	154%	110%
2	119%	108%
3	97%	90%
SAMPLE 2		
RUN #	MASS Recovery	Mutagenicity Recovery
1	105%	139%
2	107%	127%

Table II. Level 1: anion-SPE distribution of individual standards.

STANDARD	DCM	MeOH	CO2/MeOH	2% TPA/MeOH	10% TPA/MeOH
7,8-BENZOQUINOLINE	100%	-	-	-	-
PYRENE	100%	-	-	-	-
1-NITRONAPHTHALENE	100%	-	-	-	-
1-NAPHTHOL	-	25%	65%	10%	-
4-NITROPHENOL	-	-	26%	34%	40%
BENZOIC ACID	-	-	-	52%	48%
2-NITROBENZOIC ACID	-	-	-	10%	90%

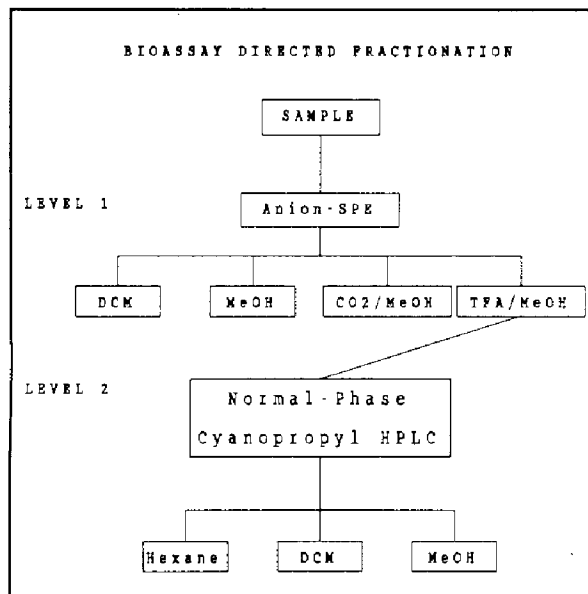


Figure 1. Schematic diagram of Bioassay Directed Fractionation.

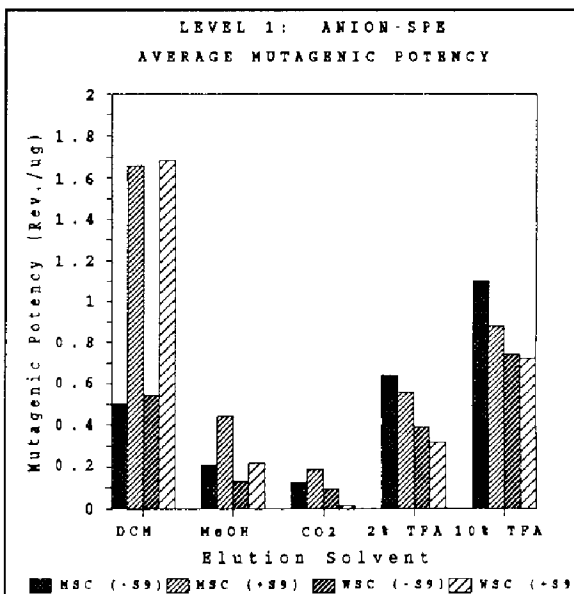
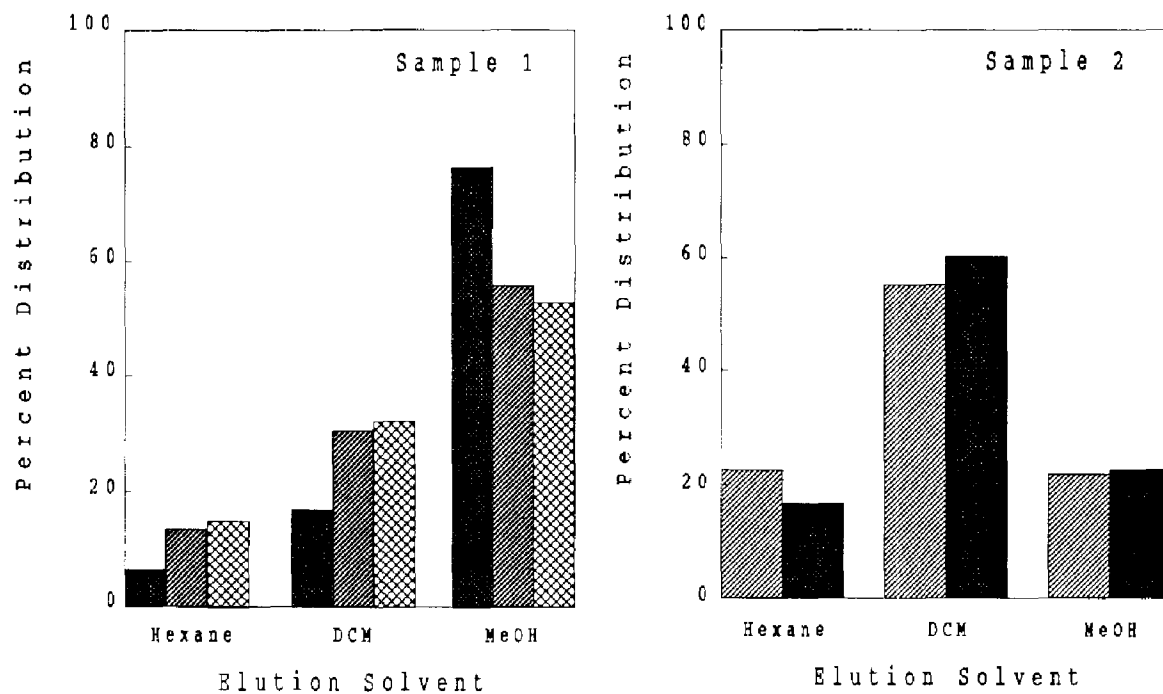


Figure 2. Average mutagenic potency from 5 anion-SPE runs.

LEVEL 2: HPLC

DISTRIBUTION OF MASS



MUTAGENIC POTENCY

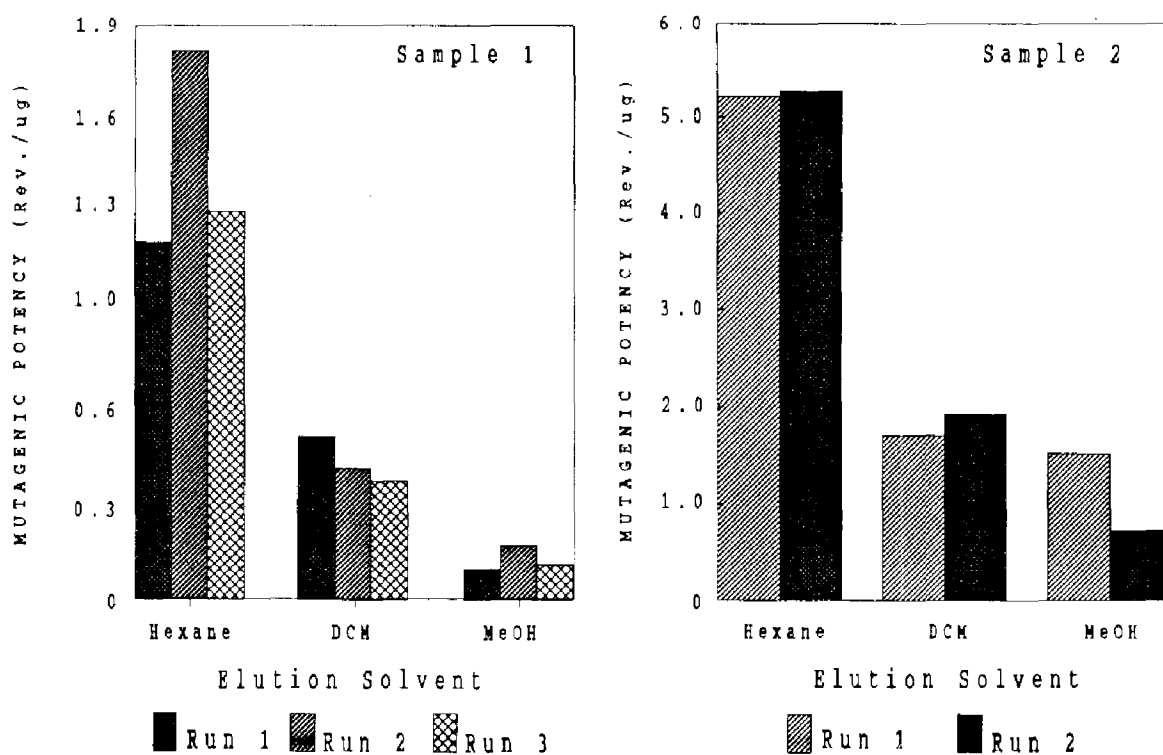


Figure 3 Second level BDF mass distribution and mutagenic potencies of samples 1 and 2.

APPLICABILITY OF GC/MS INSTRUMENTATION FOR THE ANALYSIS
OF UNDRIED AIR TOXIC SAMPLES

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Increased demand for Volatile Organic Compound (VOC) analyses of ambient air samples by Gas Chromatography/Mass Spectrometry (GC/MS) has led to the use of a variety of analytical instruments. The desire to analyze ambient samples containing polar organics such as alcohols, ketones, aldehydes, nitriles and esters can lead to the injection of a relatively large amount of water onto the analytical system. Water in the samples can cause some instruments to shut down due to pressure increases or degrade the performance of the system such that the necessary sensitivities cannot be obtained. Pleil, et.al. (1), reported the use of a Megabore column and a mass selective detector for the analysis of polar compounds, but also observed a loss of sensitivity due to peak spreading. The poor peak shape was a result of a slow temperature program to avoid an overpressure fault in the MS caused by water.

Sample moisture can be removed prior to cryogenic concentration by the use of a Nafion® dryer. Removal of moisture using a Nafion membrane does not affect the recovery of nonpolar compounds, but will restrict the analytes which can be observed (2,3). EPA Compendium Method TO-14 reports the use of a Nafion drier with a Hewlett Packard Model HP-5970 mass selective detector (4). However, this method reports that water and other light, polar compounds permeate the walls of the dryer into a dry air purge stream flowing through the annular space between the Nafion and the outer tubing. Cox and Earp (5) reported low recoveries of ketones and zero recovery of low molecular weight alcohols through Nafion membranes. They determined that other drying agents, such as potassium carbonate, also remove organic compounds.

Therefore, the analysis of polar compounds generally requires an analytical system which can tolerate a concentrated volume of water. The volume of water injected onto the system is dependent upon sample humidity

and load volume. A typical VOC analysis of a 250 mL volume of undiluted sample with 70% relative humidity results in 2 to 3 milligrams of water being introduced into the system. This amount of water is approximately 1000 times the mass of the target analytes in a typical ambient sample.

Use of turbomolecular pumped GC/MS systems with limited pumping capacity, such as the Hewlett Packard 5970 MSD, for the analysis of polar compounds in humid samples is not generally considered a viable option without the use of a jet separator and even then performance may be questionable. These systems are incapable of handling the pressure increases caused by the injection of even small amounts of water. Such systems turn themselves off when such a rise in pressure is detected. Therefore, only differentially pumped systems were considered for analysis of polar compounds. This paper discusses the use of two such systems, a Finnigan Model 4500 and a Hewlett Packard Model 5988, for the analysis of undried samples. The effect of moisture on detector sensitivity and reproducibility will be discussed. Other variables, such as the type of cryogenic focusing hardware, instrument configuration, and desorption time will also be discussed.

EXPERIMENTAL METHODS

Two approaches can be taken for the analysis of polar VOCs by GC/MS. A wide (0.32 mm i.d.) bore column can be used with the effluent directed into the source of the mass spectrometer or a Megabore (0.53 mm or larger i.d.) column and jet separator can be utilized. The wide bore column approach can suffer from the column plugging with ice causing shifting retention times, but provides better resolution. The Megabore column approach requires the use of a jet separator and has poorer resolution than the narrow bore, but does not have the ice blockage problem associated with the wide bore column and provides higher loading capacities.

Radian uses the Megabore column with a jet separator when analyzing samples for the Urban Air Toxics Program for the USEPA. A Finnigan 4500 GC/MS is used to analyze the humid samples for 38 non-polar compounds. A 0.125 inch o.d. stainless steel trap packed with silanized glass beads is used to cryotrap organic compounds from the ambient pressure samples. The sensitivity and resolution was not adversely affected by the 70% relative humidity in this standard. Reproducible retention times and correlation coefficients of greater than 0.995 are routinely obtained for these relatively nonpolar compounds.

Analysis of polar compounds has also been accomplished on this system without the use of a drier. These compounds include acetone, several alcohols, diethyl ether, 1,4-dioxane and 2-methyl-1,3-dioxolane. These compounds exhibit excellent peak shape, sensitivity and reproducibility. Using SIM techniques, estimated detection limits for 1,4-dioxane and 2-methyl-1,3-dioxolane approaching 0.5 ppbv could be obtained for both compounds. Estimated detection limits obtained in the full scan mode were much higher, on the order of 10 to 15 ppbv.

A similar GC/MS system was configured with a wide bore column (0.32 mm i.d., 1.0 μ m DB-1) to provide confirmational analysis for air samples analyzed on Radian's gas chromatography systems with multidetectors (GC/MD). The interface used on this system loaded from pressurized canisters using mass flow controllers and utilized a 0.0625 inch o.d. nickel cryotrap packed with silanized glass beads. This cryotrap is similar to the one described in Method TO-14. The column was placed directly into the source and a jet separator was not used. Excellent

reproducibility was obtained from low humidity samples. A relative standard deviation of less than 5% was obtained for one internal standard, toluene-d8, over a series of 15 analyses. Peak shape and resolution were very good for most compounds, with the exception of acetone which tailed on the DB-1 methyl silicone column (Figure 1).

Subsequent analyses of higher humidity samples on this analytical system resulted in ice plugs restricting flow through the small diameter trap. Coinciding with the ice blockage was an increased variability in internal standard response. Loading a smaller volume of sample solved the problem and allowed analysis to continue, though sacrificing sensitivity. High humidity standards formed ice plugs in the cryotrap, but did not affect peak shape or resolution (Figure 2). However, a drop in the nominal area counts for toluene-d8 from 25000 (30% RH) to 19000 occurred. Restricted sample flow through the trap corresponded with increased analytical variability.

For comparison, the interface with the small cryotrap was moved to a Hewlett Packard Model 5988 GC/MS system. Analysis of a dry standard gave excellent peak shapes and reproducibility. However, calibration with the Urban Air Toxics list of compounds at 30% relative humidity resulted in very large relative standard deviations in the response for individual compounds, as shown in Table 1. The reason for the variability in the analytes and internal standards was not understood as dry standards worked well.

Water was suspected as the cause of the problem, so mass 18 was monitored during analysis of humid samples. Figure 3 presents an elution profile of water from a 75% relative humidity sample. At 30% relative humidity, the response of toluene-d8 is reduced by 10 to 20 percent. At 75% relative humidity, the internal standard does not respond at all. The elution time of toluene-d8 coincides with the maximum of the water peak.

To prove water diminishes the detector response and the cryogenic interface is not involved in this phenomenon, a toluene-d8 standard was prepared in water and in methylene chloride so direct liquid injections could be made into the instrument. The relative standard deviation of d8-toluene in methylene chloride was 6.1% for four replicates and 64% for three replicates in water. Lowering the instrument source temperature from 250° C to 150° C did not significantly effect the variability caused by water.

Numerous attempts were made to limit the amount of water going into the mass spectrometer so the effects of water could be minimized. The interface desorption time was reduced in an attempt to limit the amount of water transferred to the GC/MS. This attempt reduced the volume of water going into the mass spectrometer, but was not adequate to obtain reproducibility at higher relative humidities. An inlet splitter was installed to divert a portion of the water before it reached the column. Limited success was obtained using this technology. A plug in the HP system used to increase the pressure during CI mode operation was removed from the source to try opening up the source so more of the water could be removed. This attempt was not successful. In addition, the filament emission current was increased from 300 uA to 400 uA in an attempt to increase ionization efficiency. This attempt also was not successful.

A jet separator was then added to the Hewlett Packard instrument so a majority of the water could be removed before being transferred into the mass spectrometer source. Monitoring for water during the analysis of a wet standard resulted in very little water being observed, as shown in

Figure 4. The relative standard deviation of repetitive analyses was 6.1% for toluene-d8 and 2.6% for bromofluorbenzene for a 65% relative humidity standard on a VOCOL 0.75 mm i.d. large bore column. However, use of the jet separator has resulted in a net loss of 20 to 50% in sensitivity (compound dependent).

The internal diameter of the cryotrap was also increased from 0.254 mm i.d. to 1.35 mm i.d. Increasing the internal diameter of the trap and leaving the first inch of the trap unpacked increased maximum load volume for water saturated standards from less than 100 mL to more than 250 mL of undiluted sample before ice in the trap started to restrict sample flow. Larger sample volumes can be concentrated using an interface similar to the one utilized on the UATMP project which loads using a vacuum source to pull the sample through the cryotrap. Load rate drops as the sample volume is increased, but does not effect the measurement of sample volume as it is determined by differences in pressure and not by a constant flow rate.

CONCLUSIONS

Analysis of undried ambient samples is best performed on GC/MS instrumentation utilizing a jet separator for the removal of water to maximize analytical reproducibility. Undried samples can be analyzed using a column placed directly into the source of the Finnigan 4500, but sample volumes must be limited if reproducibility is to be achieved. Lower sample volumes result in higher detection limits and somewhat more variable results due to fact that response may be closer to the noise level of the instrument. Large amounts of water cannot be tolerated by either instrument and a separator must be used to obtain reproducible results.

Trap design also plays an important role in the analysis of undried samples. Cryogenic concentration of samples containing 70% or more relative humidity requires a trap with an internal diameter of 1.35 mm or greater to concentrate 250 mL of sample when using an interface design based upon a consistent load rate. After this point, restricted flow results in lower load rates and irreproducible sample volumes. Use of an interface designed to load on pressure differentials allows even larger sample volumes to be concentrated.

ACKNOWLEDGEMENTS

Radian would like to thank the U.S. Environmental Protection Agency for their support of the Urban Air Toxics Monitoring Program. We would also like to acknowledge Finnigan MAT and Hewlett Packard Instruments for their support and advice in the development of these instrumental procedures.

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Table I. Relative Standard Deviations of Response Factors for Selected Compounds from Wet Standards on the HP 5988

Compound	RSD of RF (Percent)
Vinyl Chloride	19
1,3-Butadiene	5.1
Methylene Chloride	64
Bromochloromethane	72
Benzene	77
Cyclohexane	48
Cis-1,3-Dichloropropene	14
Chlorobenzene	102
o-Xylene	2.6
1,2-Dichlorobenzene	30

Low Humidity Ambient Air Sample On A 60m x 0.32 mm id
DB-1 Column - Finnigan 4500 GC/MS

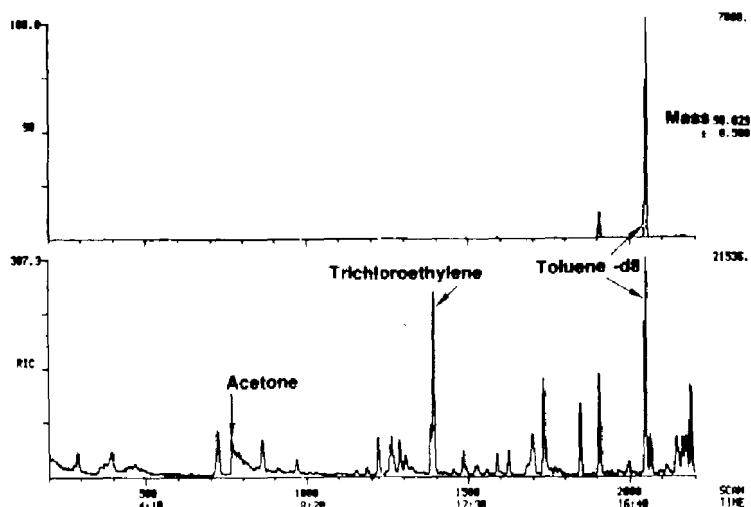


Figure 1

70% Relative Humidity Standard On A 60m x 0.32mm id
DB-1 Column - Finnigan 4500 GC/MS

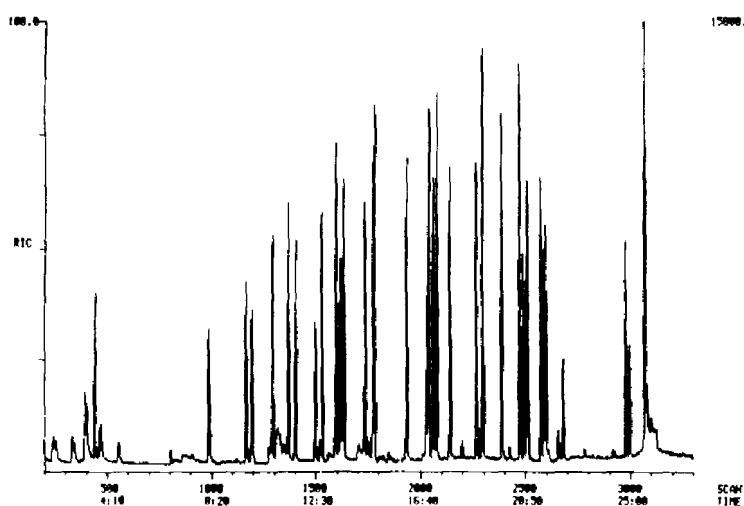


Figure 2

Elution Profile Of Water From A 75% Relative Humidity
Standard On A 60m x 0.32mm id Column-HP 5988 GC/MS

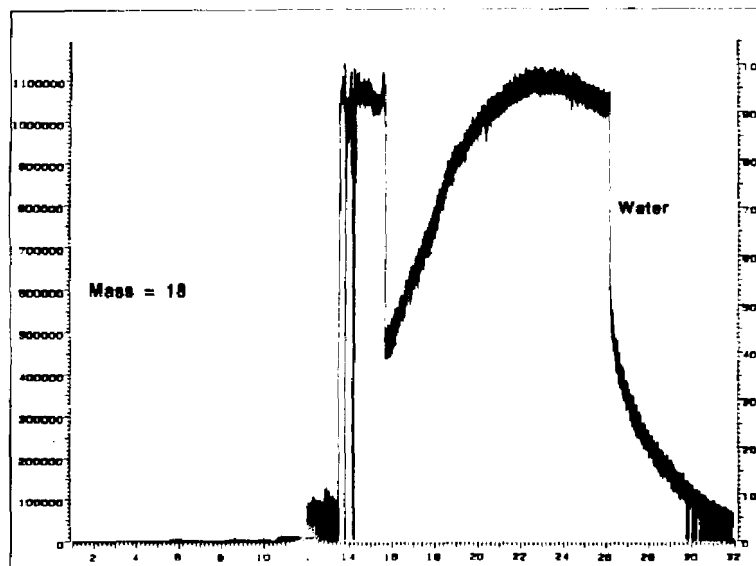


Figure 3

LABORATORY EVALUATION OF MICROSENSOR TECHNOLOGY GAS ANALYZER

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A Microsensor Technology M200 dual-column gas analyzer was evaluated for specific identification and quantitative analysis of simple and complex mixtures of organic vapors at low concentrations to assess its suitability for analysis of trace pollutants in air. Independent and simultaneous analyses were performed on nonpolar and moderately polar narrow-bore columns. Detection limits below 1 ppmv for trichloromethane, tetrachloromethane, tetrachloroethylene, benzene, and toluene were found. Relative standard deviations of retention times were less than 0.1%, but attempts to correlate data from the two columns were hampered by column bleed from one of them and by software constraints on run time.

Introduction

The measurement of volatile organic compounds (VOCs) in air is usually carried out by collecting samples at a field site and returning them to a laboratory for analysis. These samples normally have to be preconcentrated before analysis, because the typical levels of VOCs in air are too low for direct detection. This approach often results in a loss of components or inadvertent contamination of the sample.

Portable gas chromatographs (GCs) are capable of producing immediate results, with or without preconcentration, and can therefore avoid many of the difficulties associated with batch analytical approaches in a central laboratory.^{1,2} Two commercially-available GCs in this category are the Photovac 10S-series and the Microsensor Technology M200. The Photovacs use wide-bore wall-coated open tubular columns and extremely sensitive photoionization detectors that make sample preconcentration unnecessary.

These instruments have been evaluated by Berkley,^{1,2} who showed that the manufacturer's claim of a detection limit below about 0.1 part per billion (ppbv) for benzene and similar compounds is reasonable.

The Microsensor Technology M200 microchip GC contains two narrow-bore (4 m x 0.1 mm ID) fused silica columns, each of which is coated with a different stationary phase for improved selectivity.^{3,4} The instrument also includes a miniature sampling pump and injector, as well as two independent miniature high-performance thermal conductivity detectors. The two high resolution capillary columns can simultaneously analyze air samples with total run times of about 1 minute.⁴ Because the M200 gas analyzer was originally intended for industrial hygiene work, we undertook a study to evaluate its potential usefulness for ambient air monitoring, including its ability to identify and quantify toxic organic vapors in complex mixtures. This paper summarizes the results of this investigation.

Experimental Methods

The portable M200 gas analyzer contains two completely independent GC modules, each with its own miniature sample injector (injection volume 25-250 nL), column, column heater, and thermal conductivity detector (dead volume 2 nL).³ The modules share the M200's electronics and front panel controls. Method parameters, such as column temperature, injection time, and detector sensitivity can be controlled quite simply from the front panel of the instrument. The system has an automatic sampling mode which can also be activated from the front panel. For our evaluation, the M200 was configured with two 4 m x 0.1 mm ID fused silica columns: nonpolar OV-73 and moderately polar OV-1701 stationary phase coating. The different phases, and the fact that samples can be analyzed either simultaneously or independently of each other, provide a system with considerable analytical flexibility.

Besides offering control from the front panel with detector output to an integrating strip chart recorder, the instrument also offers operation via a personal computer using the EZChrom 200 software package supplied by the manufacturer. The program, which was developed to control, acquire, and process data from the M200, runs in the Microsoft WindowsTM environment.

To evaluate the M200 GC, standard gas mixtures containing benzene, toluene, trichloromethane, tetrachloromethane, and tetrachloroethylene were prepared in static glass dilution flasks at five nominal concentrations over a range from 1 to 50 parts per million (ppmv) for each compound. Besides these standards, stainless steel canisters containing 41 different VOCs at known concentrations were obtained from the Atmospheric Research & Exposure Assessment Laboratory, EPA (Research Triangle Park, NC). Three of the canisters contained all of the compounds present in the fourth canister at concentrations of about 10 ppmv. The levels of the 41 compounds in the fourth canister were between 2.3 and 4.1 ppmv.

Samples were injected into the M200 unit using either the manual or autosampler injection modes. For autosampler injection, fixed volumes of the standards were injected repetitively by connecting one end of a Teflon tube to the sample injector port and the other end to a Swagelok connector that screwed into the neck of the static dilution flask or canister.

Results And Discussion

The effect of column temperature on retention time and resolution was studied by injecting fixed amounts of the five-component standard onto the columns and varying the temperature from 30°C to 120°C. The plots in Figure 1 for the nonpolar column show a marked decrease in the retention times of the components as the column temperature is increased. The plots also illustrate the high speed of analysis achievable with the M200, especially at the higher temperatures used. Benzene and tetrachloromethane in the standard co-elute at all temperatures between 30°C and 120°C on this column but are fully resolved from one another on the moderately polar column at temperatures below 50°C. These results clearly demonstrate the usefulness of having two columns of differing polarity available in the M200 for making positive identifications of unknown VOCs.

The retention time and peak area stability of the instrument were assessed by performing replicate injections of the five-component standard mixture on both columns in the manual injection mode and the autosampling mode under computer control. As an example, Table 1 lists the retention times and peak areas obtained for the nonpolar column at 70°C. The relative standard deviations for the retention times are less than 0.1% at all analyte concentrations. The peak area precision is not as good but is generally satisfactory at higher concentrations, especially for the more volatile compounds such as trichloromethane, tetrachloromethane, and benzene. Despite higher background levels, the moderately polar column gives comparable results for retention time and peak area precision.

Detection limits were estimated by measuring peak heights of the standards as a function of concentration at different temperatures, and performing linear regression analysis. The detection limits, defined as the signal corresponding to three times the standard deviation of the baseline noise level divided by the slope of the best-fit curve, were determined for both columns and are summarized in Table 2. The results indicate that the detection limits decrease as the column temperature increases. In addition, they are about an order of magnitude lower on the nonpolar column than on the moderately polar column, due to the higher column bleed from the latter.

To assess the suitability of the instrument for the analysis of organic pollutants in air, we prepared static dilution flasks of three calibration standards of the five-component mixture (at 1, 6, and 10 ppmv) as well as two mixtures (at 4 and 8 ppmv) to serve as "unknowns". Calibration curves were prepared and used to generate peak tables, calibration tables, and timed events for the two columns at 70°C, using the EZChrom 200 data system. Then, the two "unknown" mixtures were analyzed separately on each column under the same operating conditions.

The results obtained are summarized in Tables 3 and 4. It is clear that, on the basis of retention times, positive identifications of the five "unknown" compounds can be performed with a high degree of reliability, using the calibration libraries defined by the EZChrom 200 software. There is also close agreement between measured and actual concentrations, especially at 8 ppmv. At the 4 ppmv level, the average measured values for the nonpolar column lie between 3.3 and 3.7 ppmv with relative standard deviations (RSDs) of 8-14%. For the moderately polar column, the average measured concentrations are between 3.7 and 4.3 ppmv with RSDs of 11-44%. The relatively large scatter noted here is due to the much higher background noise levels and baseline drift observed with this column than with the nonpolar column.

Attempts to extend this approach to the analysis of a complex multicomponent mixture were less successful. Three canisters containing 41 different VOCs at concentrations of about 10 ppmv each were used to generate calibration libraries for the two columns at 30°, 70°, 90°, and 110°C. This was followed by the analysis of the contents of the fourth canister, which contained all of the compounds present in the other canisters. In running these samples, we were limited by constraints on the run time imposed by the EZChrom 200 software. The maximum run time is limited by the software to 100 seconds, whereas it can be extended to 255 seconds in the manual mode. The short run time prevents the detection of later eluting peaks, especially at the lower column temperatures used. Raising the temperature to 90°C resulted in the elution of all components within the 100-second time limit, but caused a significant loss of resolution. The sample was re-run in the manual mode at 70°C and with a maximum run time of 255 seconds. This permitted the identification of several more peaks but, even under these conditions, there was considerable peak overlap, making identification and quantification of most constituents of the mixture practically impossible.

Conclusions

The Microsensor Technology M200 dual-column gas analyzer is a truly portable and useful rapid screening device that can produce valuable information about organic vapors in air. The instrument can provide independent or simultaneous analyses using narrow bore columns of different polarity and yields detection limits of less than 1 ppmv. It can be operated manually or under the control of a sophisticated, user-friendly software program. The latter, however, limits the maximum analytical run time to 100 seconds, which hampers efforts to analyze complex air mixtures of environmental interest. Work currently in progress in our laboratory is directed toward evaluating an alternative approach to improving overall sensitivity and compound specificity, based on coupling the M200 GC to an ion trap mass spectrometer.

Acknowledgement

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Table 1. Reproducibility of retention times and peak areas for nonpolar column¹ using EZChrom 200 data system

Compound	Concn. ppmv	Ave. Ret. Time (s)	Ave. Peak Area
Trichloromethane	1	20.43 ± 0.01 (0.04) ²	1041 ± 24 (2.3)
	6	20.46 ± 0.01 (0.05)	2183 ± 77 (3.5)
	10	20.46 ± 0.01 (0.05)	3071 ± 72 (2.3)
Tetrachloromethane + Benzene	1	24.99 ± 0.01 (0.04)	1652 ± 106 (6.4)
	6	25.04 ± 0.01 (0.04)	3430 ± 36 (1.0)
	10	25.03 ± 0.01 (0.05)	4844 ± 103 (2.1)
Toluene	1	43.32 ± 0.02 (0.04)	478 ± 92 (19)
	6	43.40 ± 0.03 (0.08)	1231 ± 49 (4.0)
	10	43.37 ± 0.02 (0.05)	1705 ± 23 (1.3)
Tetrachloroethylene	1	56.03 ± 0.03 (0.05)	655 ± 65 (9.9)
	6	56.14 ± 0.04 (0.08)	1506 ± 116 (7.7)
	10	56.12 ± 0.02 (0.03)	2134 ± 107 (5.0)

¹ Column temperature 70°C; ² Average of 5 measurements ± SD (%RSD)

Table 2. Limits of detection (ppmv) for five-component standard mixture

Compound	NONPOLAR COLUMN		MODERATELY POLAR COLUMN		
	30°C	50°C	30°C	40°C	50°C
Trichloromethane	0.2	0.2	2.5	2.2	
Trichloromethane + Tetrachloromethane					1.1
Tetrachloromethane			2.4	1.9	
Tetrachloromethane + Benzene	0.1	0.1			
Benzene			3.3	2.6	2.2
Toluene	0.8	0.5	9.4	6.8	4.8
Tetrachloroethylene	0.8	0.4	nd ¹	5.4	4.0

¹ nd=not detected; retention time exceeded maximum run time

Table 3. Measurement of target compounds in "unknown" gas mixtures for nonpolar column¹ using EZChrom 200 data system.

Compound	Ret. Time (s)		Concentration (ppmv)	
	Calib.	Measured ²	Actual	Measured ²
Trichloromethane	20.45	20.43 ± 0.01	4	3.4 ± 0.3
		20.46 ± 0.01	8	8.2 ± 0.4
Tetrachloromethane + Benzene	25.02	25.00 ± 0.01	4	3.3 ± 0.4
		25.04 ± 0.01	8	8.4 ± 0.6
Toluene	43.36	43.33 ± 0.02	4	3.4 ± 0.3
		43.38 ± 0.02	8	7.9 ± 0.8
Tetrachloroethylene	56.10	56.05 ± 0.02	4	3.7 ± 0.5
		56.14 ± 0.03	8	8.4 ± 0.2

¹ Column temperature 70°C; ² Average of 5 measurements ± SD

Table 4. Measurement of target compounds in "unknown" gas mixtures for moderately polar column¹ using EZChrom 200 data system.

Compound	Ret. Time (s)		Concentration (ppmv)	
	Calib.	Measured ²	Actual	Measured ²
Trichloromethane + Tetrachloromethane	24.26	24.24 ± 0.01	4	3.9 ± 0.5
		24.27 ± 0.00	8	8.3 ± 0.3
Benzene	27.15	27.14 ± 0.02	4	4.3 ± 1.9
		27.18 ± 0.01	8	8.1 ± 0.7
Toluene	49.13	49.10 ± 0.02	4	3.7 ± 0.9
		49.17 ± 0.02	8	7.9 ± 0.5
Tetrachloroethylene	56.24	56.21 ± 0.02	4	3.8 ± 0.4
		56.29 ± 0.04	8	8.2 ± 0.5

¹ Column temperature 70°C; ² Average of 5 measurements ± SD

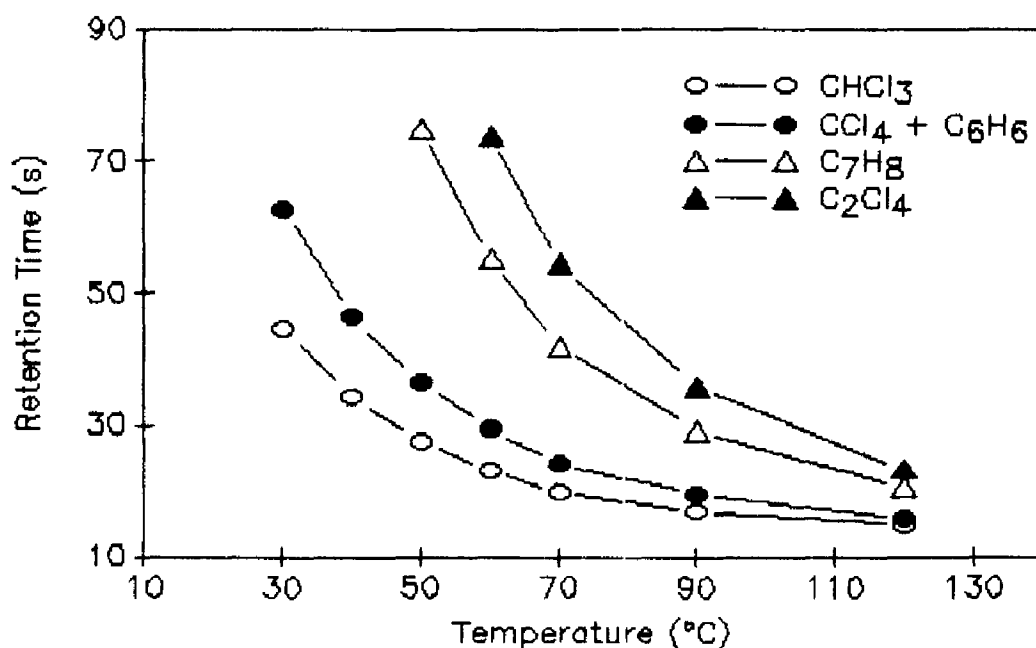


Figure 1. Effect of temperature on retention time for nonpolar column.

A REAL-TIME MONITOR FOR CHLORINATED ORGANICS IN WATER

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A low-power and portable solid-state gas sensor with a selective response to chlorinated hydrocarbons has been combined with a simple tubular silicone rubber permeator. The permeator and sensor combination have been tested in a way that simulates the on-line analysis of chlorinated hydrocarbons in water. The detection system can provide information on whether or not the sampled stream contains chlorinated hydrocarbons as well as the quantitation of the chlorinated hydrocarbon in the sample. The selective gas sensor and permeation apparatus offers a new and convenient method to analyze the contents of an aqueous sample. It is important to note that the approach allows the use of a gas sensor to analyze a liquid stream in near real-time. Since many more types of gas sensors are available than liquid sensors, this approach may be more generally useful if other gas sensors are interfaced to the liquid sampling system by means of semi-permeable membrane technology.

This analytical method combines a selective permeator and a portable gas sensor. The new approach may find use in field screening of mud, water, or other complex sample matrices for volatile halogenated organic compounds.

INTRODUCTION

Chlorinated hydrocarbons are potentially toxic vapors that commonly occur in the workplace, environment, and process stream. Recently, the Environmental Protection Agency has added 25 organic chemicals to the list of compounds regulated as toxic in wastes under the Resource Conservation & Recovery Act¹. Sixteen of these organic chemicals are chlorinated hydrocarbons and are illustrated in Table I. It is important and useful to develop a real-time, inexpensive analytical method for the determination of chlorinated hydrocarbons in waste water.

Chemical sensor technology is playing an increasing role in analytical science. It not only provides real-time, on-site information about the presence and concentration of chemicals in a given environment, but also is a less expensive alternative to large analytical instruments. Unwin and Walsh² have described a sensitive chlorinated hydrocarbon sensor which is based on the electrical conductivity change effected by the adsorption of chlorine, produced by decomposition of the chlorinated hydrocarbon over a heated platinum coil, on films of lead phthalocyanine. This paper describes a rare-earth sensor that is selective for chlorinated hydrocarbons.

Membrane technology is developing significant uses in the analytical sampling systems. It not only can be used to extract or separate organic vapors from an aqueous sample matrix, but also offers a technique for continuous sampling. Hellgeth and Taylor³ have described a membrane based method for on-line high-performance liquid chromatography/Fourier transform infrared spectrometry. This method involved the detection of the organics in an aqueous/organic segmented stream through a flow cell which is constructed by using multiple layers of Teflon membrane. Blanchard and Hardy⁴ introduced a separation method based on the permeation of volatile organic compounds through a silicone polycarbonate membrane from an aqueous sample matrix into an inert gas stream. A portion of this stream was then injected into a capillary gas chromatograph. Melcher⁵ developed a silicone membrane flow injection system for the determination of trace organic compounds in aqueous samples. Recently, Lauritsen⁶ reported using a silicone membrane for on-line monitoring of dissolved, volatile organic compounds with mass spectrometry.

Combining membranes and chemical sensors will allow the development of new in situ detection and quantification methods for pollutants and trace chemicals in waste water. Our previous paper⁷ presented the possibility of the use of a rugged permeation membrane in combination with a low cost, small, selective gas sensor for on-line and near real-time analysis of chlorinated hydrocarbons in an aqueous phase. This paper

will focus on the feasibility of this real-time monitor for the determination of chlorinated hydrocarbons such as chlorobenzene, 1,1,1-trichloroethane, chloroform in water.

EXPERIMENTAL METHODS

Sensor

A schematic diagram of the sensor is shown in Fig. 1. A dc potential of about 4 V across the electrodes is maintained and the conductance is measured using Ohm's law and the voltage drop across a known resistor. In absence of a chlorinated hydrocarbon vapor, a high resistance is observed and the conduction between terminals 1 and 6 is very small. But in the presence of a chlorinated hydrocarbon vapor, the resistance decreases significantly and this increases the current flow between the terminals. The magnitude of the sensor background current at constant dc bias voltage is very sensitive to the presence of chlorinated hydrocarbon vapors in the atmosphere surrounding the sensor since these gases alter the conductance of the semiconductor surface. This conductance change in the presence of chlorinated hydrocarbon vapors is the analytical "signal" from this sensor, i.e., the conductance is a function of the concentration of the chlorinated vapor present. The sensor is insensitive to many hydrocarbon contaminants such as benzene, hexane and can be operated in air.

Permeator

Since the chlorinated hydrocarbon sensor is a gas sensor, it is necessary to convert the aqueous sample containing the analyte into a vapor sample suitable for analyses by the gas sensor. The permeation cell has been described⁷ and consists of thin wall permeable tubing (Silastic Medical-Grade Tubing, 0.012 in. i.d. x 0.025 in. o.d. manufacture by Dow Corning) that is submerged in the aqueous sample. Silicone materials preferentially allow organic compounds to permeate while rejecting water and other highly polar molecules.

Instrumentation

The experimental system schematic is given in Fig. 2. The microprocessor was used to record the experimental data and to control the sensor and the sample exposure time. The collected data are analyzed by the PC computer to provide a graphic display of the results. In order to measure the net response for organic compounds we used two permeation cells. One is submerged in clear water for the sensor baseline. The other is in water containing the organic compound at a low concentration. The two permeation cells were purged with the same flow of air carrier gas and connected to a three-way solenoid valve that

was placed in front of the gas sensor inlet. The solenoid valve is controlled by a microprocessor. By switching the valve it was possible to make a very fast change of air flow over the sensor from pure water to sample. The flow rate was maintained constant at 170 cc/min during the experiments.

RESULTS

At constant temperature the conductivity of sensor bead changes with the partial pressure of the analyte⁷. This pressure dependence of conductivity of takes the form

$$\sigma/\sigma_0 = k P^m \quad (1)$$

for chemisorption on a transition-metal-oxide system, where σ is the conductivity, P is the partial pressure (or gas concentration) of the reacting gas, k and m are constants. Since the ratio of the conductivities, σ/σ_0 , is equal to the ratio of the conductances, C/C_0 , equation (1) can be written as

$$\ln C/C_0 = \ln k + m \ln P \quad (2)$$

In this paper, we use the ratio of the conductance of air containing sample to that of clean air, C/C_0 , as the sensor signal. The sensitivity of the chlorinated hydrocarbon sensor is highly dependent upon the sensor temperature and gas flow rate⁷.

A series of different low concentrations (0.5-10 ppm) of chloroform in water were prepared, and the signals are given in Fig. 3. Three different chlorinated hydrocarbons, chloroform, chlorobenzene, and 1,1,1-trichloroethane, in water were (individually) analyzed by using this monitor (see Fig. 4). The responses at different low aqueous concentrations (0.5-10 ppm) were recorded by using an amplifier with a gain of 100 to boost the signal. There is a good linear relationship between the response for all three chlorinated compounds and the concentration and the results of the regressive analysis is given in Table II. This linear response was obtained using the simple silicone tube permeator and the entire benchtop instrument system.

Fig. 5 presents the selectivity of the chlorinated hydrocarbon sensor. Three chemicals, chlorobenzene, benzene, and hexane with the same concentration (100 ppm in a gas phase air mixture) were detected by the same sensor. There is a great difference in sensor response between chlorinated and unchlorinated hydrocarbons. We estimate that the response to chlorinated hydrocarbons is at least 10^3 and perhaps 10^5 times greater than for hydrocarbons. The origin of this unusual selectivity is not completely understood at this time.

The lifetime of this sensor is suitable for practical application (see Fig. 6). The life of this small inexpensive sensor is over 20 days with continuous exposure to high concentrations of chlorobenzene vapor. This is more than 2,000 sample analyses at high concentration. The stability of sensor response can be found in Fig. 7 and sensor is quite stable over a day with variations of about 10% and stable over its entire lifetime with variation in sensitivity of less than 50%. The lifetime appears to be a function of the concentration exposure history of the sensor and, perhaps, would be greatly improved if used at lower levels of sample.

CONCLUSIONS

The chlorinated hydrocarbon sensor and permeator system has high sensitivity and selectivity and can be used for the determination of chlorinated hydrocarbons in aqueous samples. We have examined concentrations between 500 ppb and 10 ppm. Lower levels may be possible with a higher gain amplifier. Using a semipermeable membrane allows the application of relatively inexpensive gas sensors to the analysis of liquid samples. The relatively low cost, small, and rugged equipment needed for this analysis has the potential for continuous on-line analysis of aqueous streams as well as the field screening of water samples. The sensor is quite stable over its entire lifetime. The simple silicone permeation tube is rugged, resistant to many chemicals, and easily inserted into a concentrated (acid, base, etc) water stream and can provide the analyte to the gas sensor in a form suitable for quantitative analysis.

Further work will be focused upon understanding the sensor mechanism. In addition, optimum geometry for the permeation system will be investigated to improve the analytical performance of the sampling system. The characterization of the analytical method will be extended by using field samples as well as laboratory standards.

ACKNOWLEDGEMENTS

We wish to acknowledge the funding for Mr. Cao from Dow Chemical Company and the inciteful comments of Dr. Robert Bredeweg on this work, especially for suggesting the silicone membrane technology for the permeator.

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Table I. These organics in wastes will be regulated as hazardous by EPA.

Samples	Regulatory level (mg per L)
Benzene	0.5
Carbon tetrachloride	0.5
Chlordane	0.03
Chlorobenzene	100.0
Chloroform	6.0
o-Cresol	200.0
m-Cresol	200.0
p-Cresol	200.0
1,4-Dichlorobenzene	7.5
1,2-Dichloroethane	0.5
1,1-Dichloroethylene	0.7
2,4-Dinitrotoluene	0.13
Heptachlor	0.008
Hexachlorobenzene	0.13
Hexachloro-1,3-butadiene	0.5
Hexachloroethane	3.0
Methyl ethyl ketone	200.0
Nitrobenzene	2.0
Pentachlorophenol	100.0
Pyridine	5.0
Tetrachloroethylene	0.7
Trichloroethylene	0.5
2,4,5-Trichlorophenol	400.0
2,4,6-Trichlorophenol	2.0
Vinyl chloride	0.2

Table II. Least-Square Regression Results from Fig. 4.

samples	slope	y int	R ²
chloroform	0.5379	0.5043	0.997
chlorobenzene	0.5814	0.6280	0.988
1,1,1-trichloroethane	0.7226	0.6890	0.993

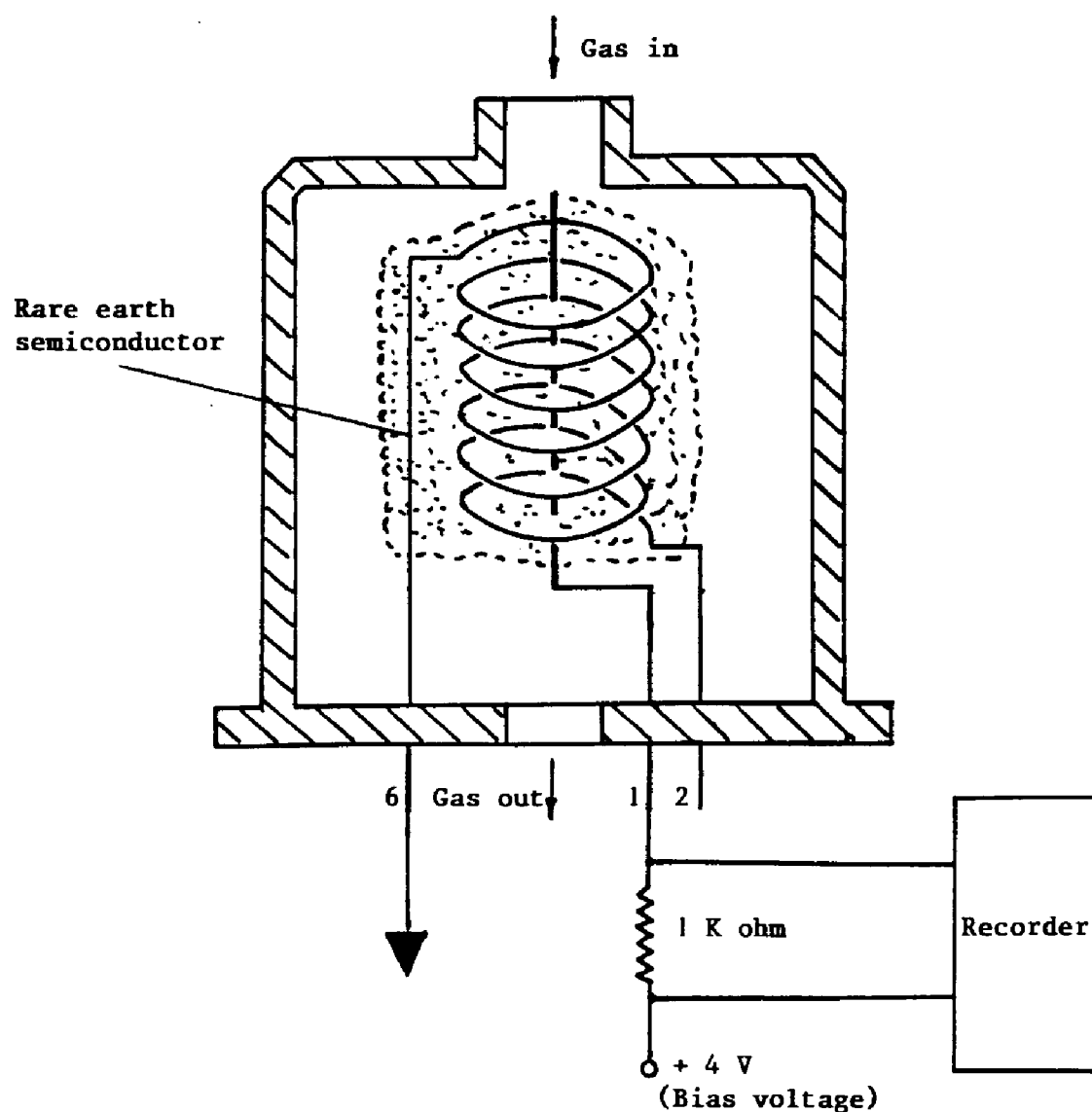


Figure 1. Schematic diagram of sensor and conductance measurement circuit.

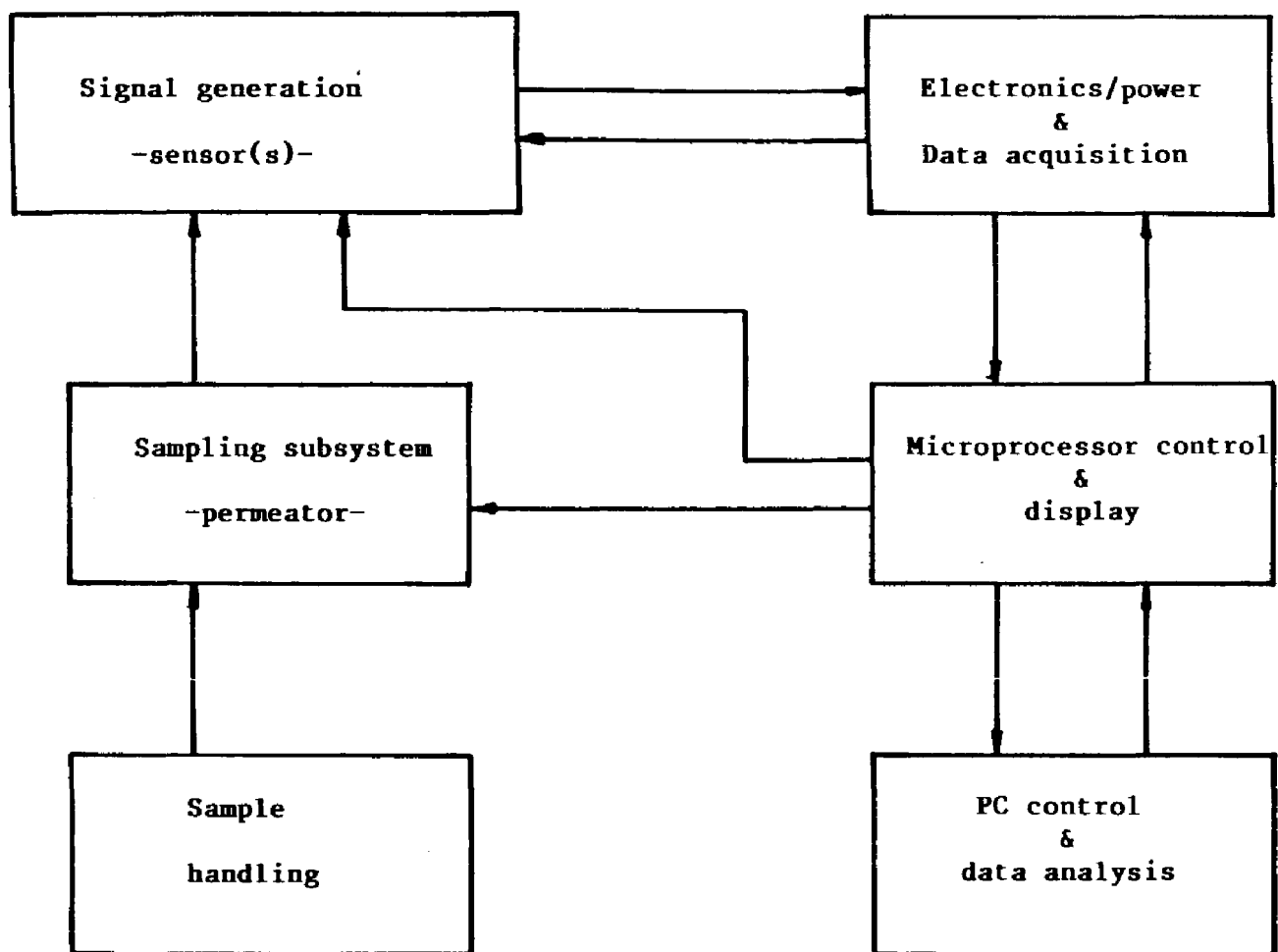


Figure 2. Schematic functional diagram of the experimental apparatus.

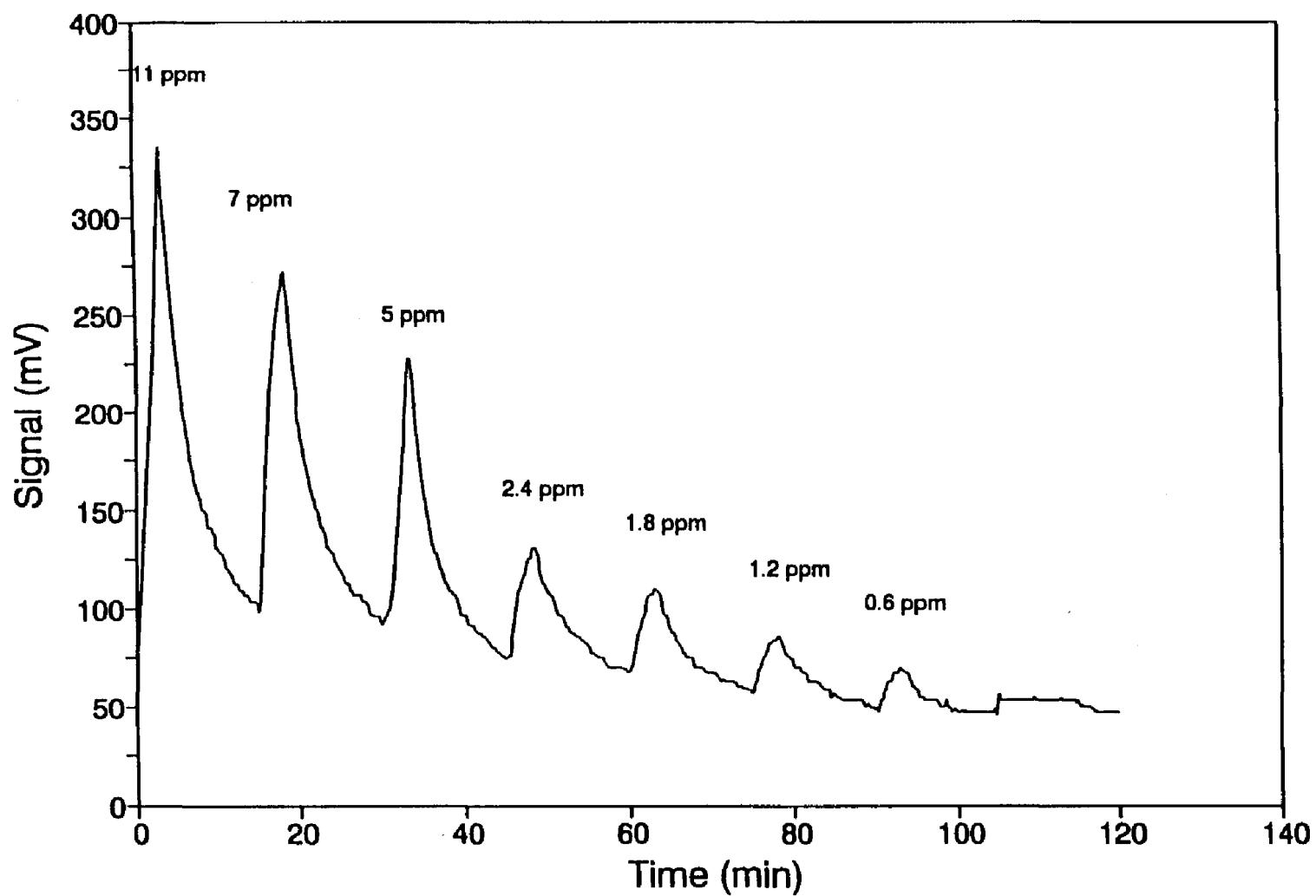


Figure 3. Examples of 3-minute exposures of the sensor to the permeator containing chloroform analyte at different concentrations separated by 17-minute to the permeator containing clean water.

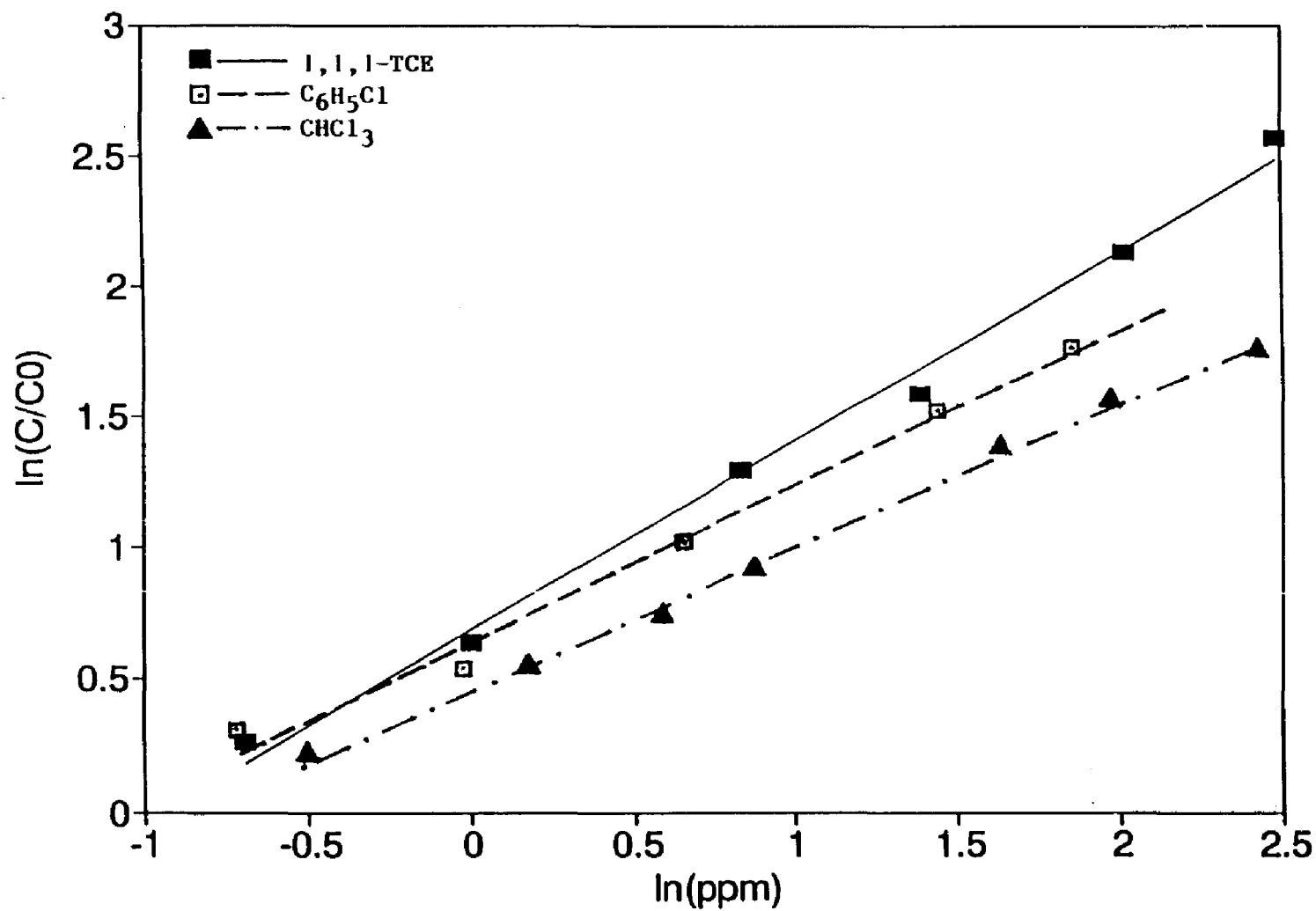


Figure 4. Example of the relative (linear) sensitivity of the sensor to aqueous concentrations of three analytes.

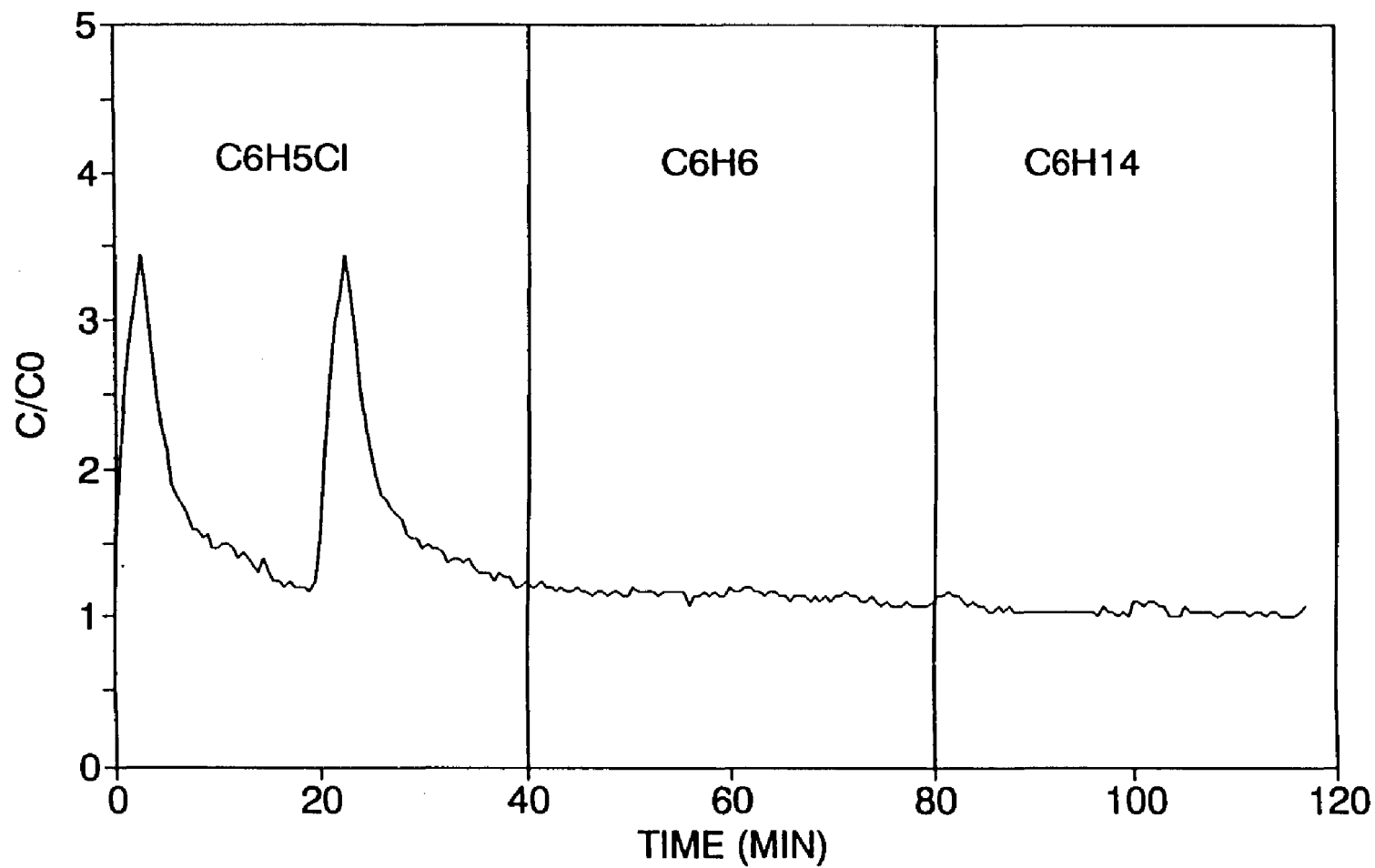


Figure 5. Example of the selectivity of the sensor for chlorinated organics versus aliphatic or aromatic hydrocarbons.

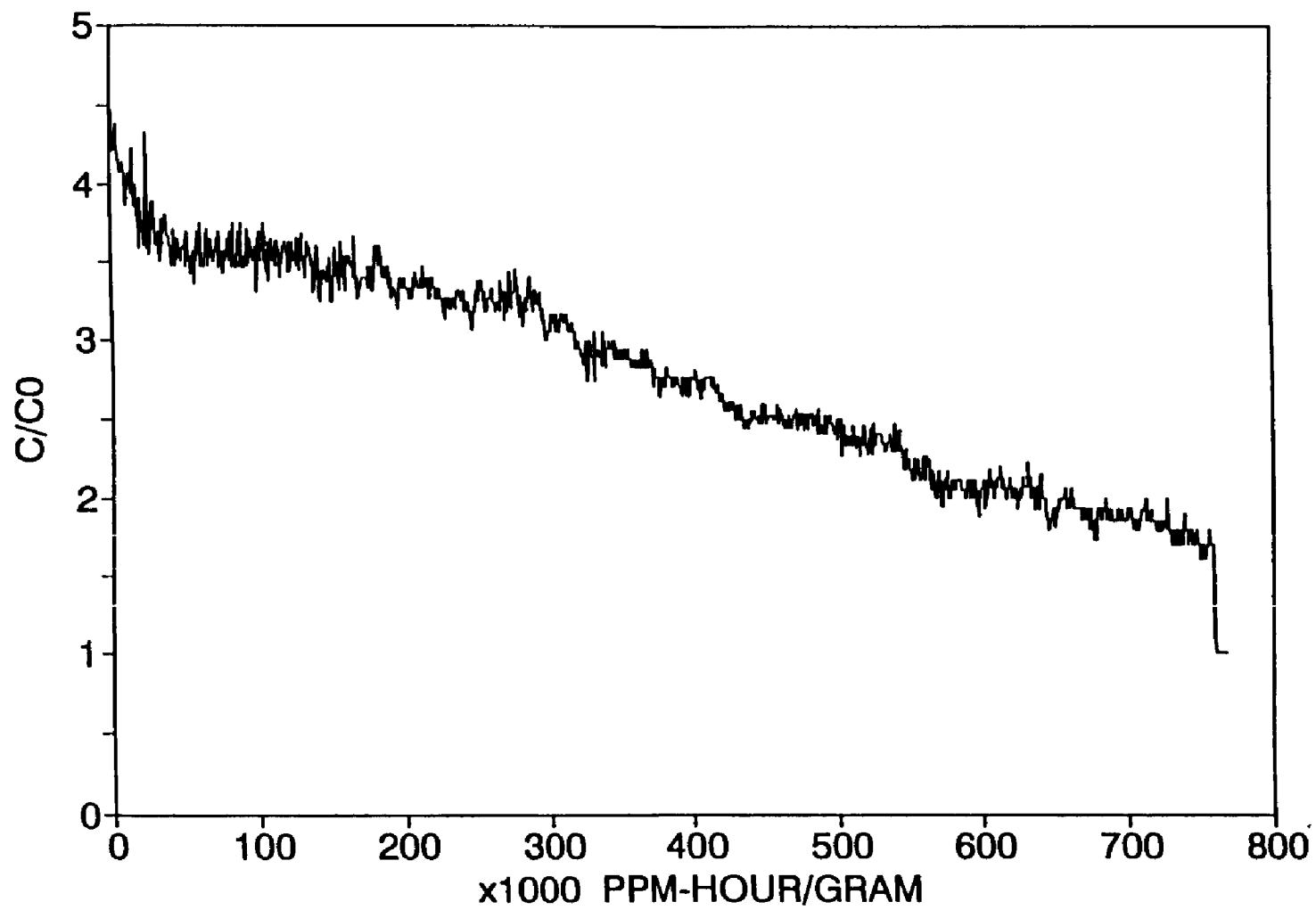


Figure 6. Sensor lifetime as a function of sensor exposure to analyte and sensor size.

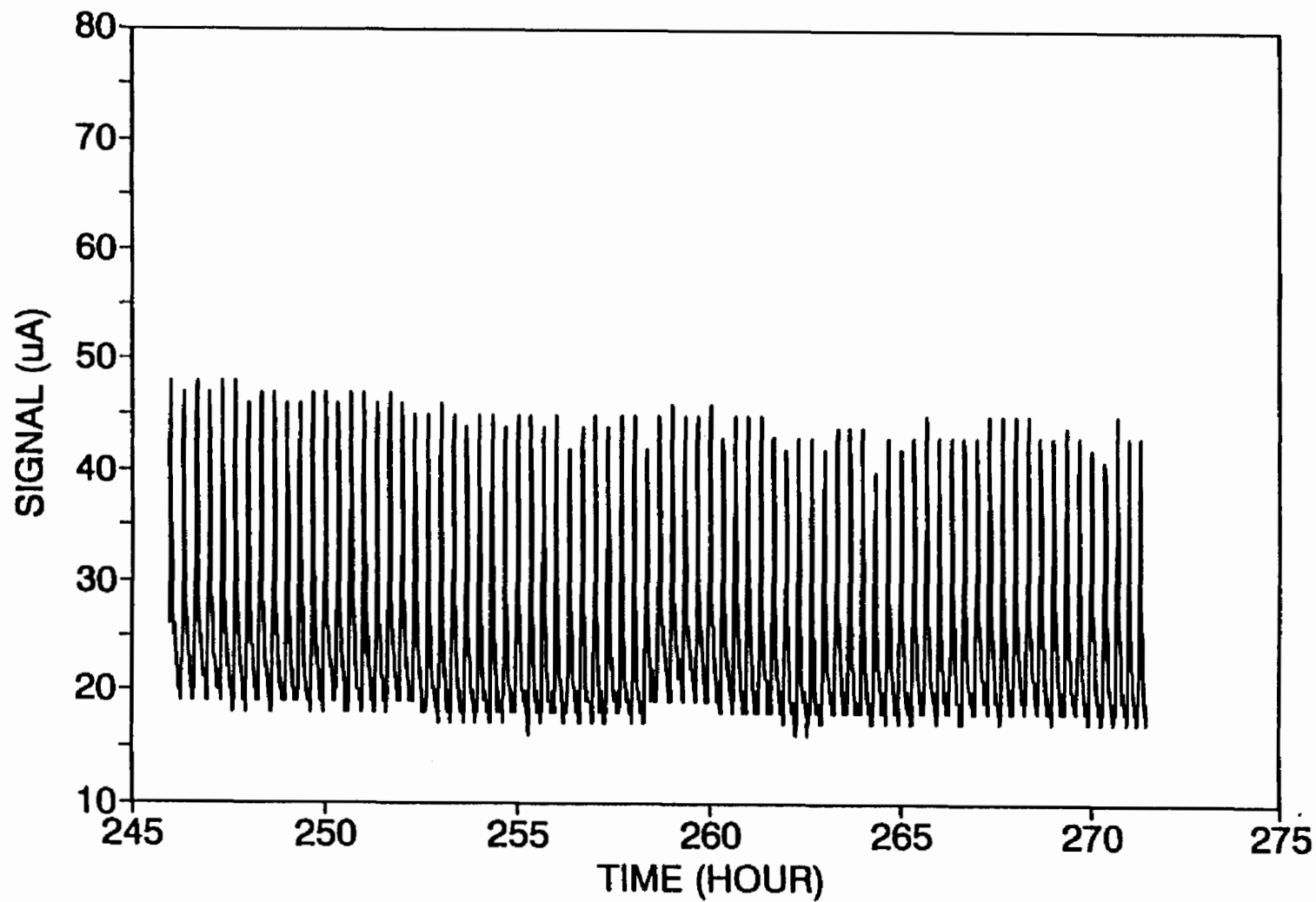


Figure 7. Short term (1-day) stability of the sensor response. Repeated injections (3-minute exposures) of 100 ppm chlorobenzene in air.

PERFORMANCE OPTIMIZATION OF PHOTOVAC
10S70 PORTABLE GAS CHROMATOGRAPH

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Photovac portable gas chromatographs (PGC) are designed to automatically sample ambient air for industrial hygiene analyses in which typical analyte concentrations are a few parts-per-million (volume/volume). However, the photoionization detectors used are extremely sensitive to benzene and its homologues, to ethylene and its homologues, and to their halogen-substituted derivatives. Such compounds can be detected by PGC's at low part-per-billion levels without preconcentration. To do this successfully, operating procedures which are suitable at higher concentrations must be modified. These modifications, rationales for them, and examples of their application are discussed.

Introduction

Photovac portable gas chromatographs (PGC) use photoionization detectors that are extremely sensitive to compounds which have ionization potentials lower than 10.6 electron-volts and are volatile enough to elute from an isothermal column at 50°C or below. Included are benzene, ethylene, their homologues, and their halogen-substituted derivatives, all commonly-occurring toxic air pollutants (1-3). Preconcentration is not required to detect these compounds at part-per-billion (volume/volume) levels, so many sampling errors which might affect preconcentration-based methods can be avoided. Data are obtained in near real-time, which facilitates rapid screening of emission sources. However, these PGC's were originally intended for industrial hygiene analyses in which analyte concentrations typically exceeded one part per million. Using them at one part per billion or less requires modified operating procedures which are discussed herein.

Experimental

Two Photovac Model 10S70 PGC's equipped with constant-temperature column accessories were used. A 0.53 millimeter inside diameter X 10 meter long methylsilicone-coated open-tubular column was used to analyze compounds of intermediate-to-low volatility. A KCl/Alumina porous-layer open-tubular column of the same size was used to analyze more volatile compounds. Ultrazero air (less than 0.1 part per million carbon) was used as carrier gas, and high-purity helium was used to clean columns. A sample inlet probe consisting of 2 millimeter inside diameter X 9 meter long stainless steel tubing was extended from the "SAMPLE IN" port of the PGC through a vehicle window to a point at least 2 meters above ground. Calibration standards prepared by flow-dilution of commercial 10 part per million mixtures of organic compounds in nitrogen (Scott Specialty Gases) were pumped into 6-liter passivated canisters to a positive pressure of about 100 kiloPaschals (25 pounds per square inch gauge) using a metal-bellows pump. Data were stored on disk by IBM-compatible laptop computers using Photovac DANDI (Data Acquisition and Disk Interface) software.

Results and Discussion

Power Requirements

Photovac PGC's were originally powered by an internal 12 volt battery which recharged automatically when the unit was connected to 110 volt mains. An auxiliary 12 volt battery could be connected to extend operation time. Twelve ampere-hour gel-cell battery packs (Globe Battery Division, Johnson Controls) lasted about 6 hours, provided they were in good condition and fully charged at start-up. The constant-temperature column accessory increased power consumption significantly, so that 12 ampere-hour gel-cells discharged much sooner. Although gel-cells may be recharged many times, a single deep discharge can ruin them, and such damage is not immediately apparent. A panel volt-meter attached to the power lead is recommended for monitoring battery performance, since external battery voltage is not otherwise displayed, and much time could be lost by trying to operate with a dead external battery. Larger gel-cells (80 ampere-hours) last more than 24 hours and consequently are more reliable. Marine batteries (100 ampere-hours), which are tolerant of deep discharge, may also be used. Gel-cells can be shipped by air, but marine batteries cannot.

Column and Valve Contamination

Operating at high gain (typically 200 or higher) to detect ambient background levels of pollutants results in a split-level baseline because trace contaminants bleed from solenoid valves when they are energized. When the valves de-energize to resume backflush the baseline falls to its original level. This disruption lasts about a minute, during which eluting peaks cannot be quantitated, so the time when backflush resumes must not be too near retention times of target compounds. Also, if backflush resumes too early, late-eluting compounds may be partially lost and not detected. Because of this, the backflush portion of the sampling cycle must generally be too short to clear less-volatile compounds from the precolumn or to prevent their breaking through into the analytical column. As a result, column bleed gradually increases until visible baseline drift appears. Eventually the baseline buckles as backflush resumes, and finally it drops below zero at that point and disappears from the strip chart. Usually it will have returned to a positive value by the end of the chromatogram, so it has a large positive slope between resumption of backflush and the end of the chromatogram. Incorrect placement of integration baselines by the microprocessor is more likely to occur with a sloping baseline, especially if the slope is positive. The only remedy for such "bad integrations" is

to retrieve chromatograms stored on disk and correct them manually, using the "BASELINES" feature of DANDI, a tedious procedure which requires saving the corrected chromatogram to a separate file. Large volumes of data can be damaged in this way, and for a long time the cause of the problem was believed to be failure of solenoid valves. We have found it effective to bake columns in a drying oven at 90°C for 4 hours while backflushing with helium, but drying ovens are not field-portable. One of us (Kronmiller), after conferring with Photovac, designed and built a portable column heater which uses a strip of heating tape around the outside edge of the column to heat it. Four temperature sensors, built into the column assembly, are used to control thermal output. The unit is powered by 110 volt mains, and it is about half the size and weight of a briefcase.

Detection Limits

An analytical detection limit is usually taken to be the quantity of a compound which produces a signal just large enough to be distinguished from baseline noise. Criteria for this distinction are not widely agreed upon, but the microprocessors in Photovac PGC's don't process peaks smaller than 5 millivolt-seconds. This clearly defines a theoretical detection limit for each compound at each gain level. It is the quantity sufficient to produce a peak with 5 millivolt-second area. However, the real detection limit could be higher because the microprocessor does not reliably notice small peaks when the baseline is not level.

Data Handling

Mobile monitoring in a vehicle is an important use for PGC's, but they generally produce more data of higher quality by stationary autosampling. Sampling at 15-minute intervals round the clock produces large volumes of data which must be validated and tabulated. Sample files can be copied from floppy disk to a virtual disk in computer memory to facilitate rapid screening for improper integrations and other problems using the "LIST AUTO VIEW" feature of DANDI. Quantitation lists can be printed for manual data tabulation, or data can be copied directly from the computer screen or plotter tape to a table, but it is safer not to risk scrambling data by passing them through a human brain. The DANDI "EXPORT TO TEXT" feature can be used to output from each sample file an ASCII text file which can later be imported to a Lotus 123 spreadsheet. Individual sample files must be manually retrieved and assigned filenames to accomplish this. Once imported into Lotus, they can be edited and saved as worksheet files. One of us (Berkley) has written a Lotus macro which automatically imports ASCII files one-by-one from a filename list, removes unneeded portions, transposes from linear to columnar format, and saves them as Lotus worksheet files. Macros for combining a list of these worksheet files into tables of concentrations or retention times were also written. These macros require Lotus 123, Version 2.01 or higher. They can be modified to suit the needs of individual users. They are not protected by copyright, and interested parties may request copies of them.

Calibration Libraries

New operating conditions were devised to expand calibration libraries to maximum capability of the PGC. The methylsilicone column at 40°C, 6 milliliters per minute, and gain 200, was used for compounds of intermediate volatility. The same column at 50°C, 17.7 milliliters per minute, and gain 500, was used to analyze less-volatile compounds, including isomers of trimethylbenzene and dichlorobenzene. The KCl/Alumina column at 40°C, 12 milliliters per minute, and gain 1000 can be used to analyze highly volatile compounds such as vinyl chloride and vinylidene chloride.

Low Temperature Operation

The extent to which winter temperatures might tax battery capacity or impair column temperature stability was investigated. No difficulty was found during all-day operation above 0°C when equipment was taken outdoors and energized while still warm. However, responses to airborne compounds of intermediate-to-low volatility began to diminish near 10°C, apparently due to sample condensation on the inlet tube. Concurrent canister samples, taken for comparison, did not pass through an inlet tube. Data in TABLE 1 show results of concurrent PGC and canister sampling at different temperatures. At 7°C the PGC found less of each compound than did the canisters. At higher temperatures the two methods were in better agreement. It should be remembered that canister and PGC samples are not equivalent, because the PGC analyzes one of seventy milliliters of air which enter the sampling probe, while a representative sample is analyzed from the entire six liters which enter the canister during the same period. Usually canister and PGC samples resemble each other closely, but concentrations in air downwind of a point source (such as a dry cleaning plant) may be nonhomogeneous and can lead to significant discrepancies, as seen in TABLE 1. Concurrent PGC and canister samples for less-volatile compounds are shown in TABLE 2. The PGC apparently responded to an unknown compound which coeluted with m,p-dichlorobenzene and 1,2,4-trimethylbenzene.

Retention Time Precision

We have previously shown, for a single series of runs, that the constant-temperature column accessory can reduce relative standard deviations of retention times at constant carrier flow by an order of magnitude to about 1% (4). However, rotameters were inadequate for duplicating carrier flow rates from one series of runs to another. A digital bubble meter, which can measure flows to within 0.1 milliliter per minute, worked much better. It also revealed that a rotameter attached to the chromatograph can cause fluctuations in carrier flow. The rotameter ball remained perfectly steady while carrier flow varied continuously over a range of half a milliliter per minute. Removal of the rotameter reduced fluctuation to less than 0.1 milliliter per minute. Setting a preselected flow accurately (within 0.1 milliliter/minute) is still difficult because the 3 needle valves which control it perform erratically, but patience can be rewarded by day-to-day retention times of good precision. TABLE 3 shows 5 series of sampling runs during a month in late winter. The data came from two PGC's equipped with similar columns. Such precision makes it possible to interchange libraries. A library saved to disk from one PGC can be used in another, a useful option in case of emergency, but not a recommended procedure for routine operation.

Conclusions

Photovac portable photoionization gas chromatographs produce valid results which compare reasonably well with other methods when adequate operating procedures are followed. To get good results, battery power must be sufficient, columns must be clean, flow rates must be properly set, the sample intake line must be clean and reasonably warm, and accurate calibration standards must be used.

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Disclaimer

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TABLE 1. CONCURRENT PGC AND CANISTER SAMPLES
AT SEVERAL AMBIENT TEMPERATURES

	Tri chloro- Benzene	ethene Toluene	Tetra- chloro- ethene	Chloro- benzene	Ethyl- benzene	m,p- Xylene	o- Xylene	
Monday February 26, 1990. 7°C. Mall below parking deck.								
PGC	1.29	ND	ND	0.56	ND	ND	0.78	ND
Canister	2.10	ND	2.90	3.90	0.50	0.60	1.20	0.70
Monday February 26, 1990. 18°C. Dry cleaning plant.								
PGC	ND	ND	ND	29.05	ND	ND	ND	ND
Canister	0.50	ND	0.50	9.40	ND	ND	0.30	ND
Friday March 26, 1990. 28.3°C. Dry cleaning plant.								
PGC	ND	ND	ND	1.41	ND	ND	ND	ND
Canister	0.68	ND	0.56	3.38	ND	< 0.20	0.35	0.20
PGC	ND	ND	ND	4.09	ND	ND	ND	ND
Canister	0.76	ND	0.62	3.15	< 0.20	< 0.20	0.29	< 0.20

TABLE 2. CONCURRENT PGC AND CANISTER SAMPLES
OF LESS-VOLATILE COMPOUNDS

Monday March 12, 1990. 20°C. Mall below parking deck.

				m,p-Dichloro- benzene or 1,3,5-Tri- methylbenzene or 4-Ethyltoluene	1,2,4-Trimethyl- benzene or Benzylchloride	o-Dichloro- benzene
	o-Xylene	Bromobenzene				
PGC	0.10	0.01		0.04	13.17	ND
Canister	0.35	ND		ND	<0.20	ND
PGC	0.03	0.03		0.37	11.07	ND
Canister	0.25	ND		ND	0.29	ND
PGC	0.22	ND		0.72	10.51	ND
Canister	0.45	ND		<0.20	0.68	ND

TABLE 3. RETENTION TIME STABILITY DURING FIVE DAYS OF SAMPLING
BETWEEN FEBRUARY 22 AND MARCH 23, 1990.

Ambient Temperature Range 7 - 30°C.

	Benzene	Trichloro- Ethene	Chloro- benzene	Ethyl- benzene	m,p-Xylene	Styrene	o-Xylene
Runs	32	32	32	32	32	32	32
Peaks	13	4	6	12	22	3	13
Mean	128.7	165.1	489.6	567.2	606.1	688.5	735.0
SDEV	2.3	3.5	16.4	19.1	18.5	5.5	18.8
%SDEV	1.8	2.1	3.4	3.4	3.1	0.8	2.6

COMPUTER SOFTWARE FOR GAS CHROMATOGRAPHY IN THE FIELD

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The availability of small, portable gas chromatographs makes their use at or near the site of sample collection an attractive prospect. Such systems can be used for real-time diagnostic purposes, for sample screening or a combination of both.

The computer hardware requirements of data acquisition and processing have long been in the range satisfied by off-the-shelf desk-top and lap-top computers. The state of the art in chromatography software, however, is not so advanced. Commercially available software packages are designed to operate in a laboratory and require considerable support and supervision from the laboratory staff. Under field conditions, the time of the qualified staff available is too valuable to be allocated except where necessary and may be unavailable altogether. The authors have developed and are currently testing a software package that minimizes its need for the supervision of qualified analytical staff.

The three areas of most concern in chromatography software are the peak-picker/integrator, the analyzer and the calibrator. In the case of the integrator, most of the need for supervision has been eliminated by using improved algorithms. The two most troublesome aspects of user supervision in chromatographic integration, integrator events and slope sensitivity settings are entirely dispensed with. Identification is accomplished by game-playing to make optimal, feasible identifications based upon elution time on two columns, relative peak size and known elution order. Where possible, coelution is accounted for. The calibrator reduces the calibration process to a relatively intuitive "point-and-click" process and supports both single-point and multi-point calibration in a logically consistent manner.

Introduction.

The cost of laboratory analysis, in terms of both dollar cost and turn-around time make field analysis, where possible, an attractive alternative. It may be that the general character of a site can be assessed more quickly and efficiently using field methods and, once that is known, a more efficient sampling strategy may be established to collect the samples that need be sent to a contract laboratory. Even in cases where preliminary analysis is not used, it may still be efficacious to screen collected samples in order to determine which ones should be sent to a contract laboratory. Where volatile organics are of concern, gas chromatography is often the method of choice. Accomplishing chromatography in the field means that a chromatograph and its associated data system are operated outside the laboratory environment for which most chromatographs and data systems were designed. The absence of laboratory support necessitates changes to both the gas chromatograph and its data system hardware and software.

The necessary hardware changes have already been accomplished by chromatograph and computer manufacturers. There are several portable or transportable gas chromatographs such as those manufactured by PhotoVac and by Microsensor Technologies. Portable and transportable computers have been in use since the late 1970's and simple MS/DOS-based machines are now under 5 pounds. Advanced systems that are being used as gas chromatographic and mass spectral data systems, such as the Toshiba 3200 and Macintosh Portable are under 18 pounds.

Gas chromatographic data system software, however, has not changed significantly since the late 1970's. It has not had to change, being well suited to its target environment, an analytical laboratory. The main aspect of this environment from a programmer's point of view is that there are staff available whose job it is to see that their equipment, both hardware and software, work properly, including providing the software with whatever data that it needs to function. In the case of gas chromatography, this includes partial descriptions of the chromatograms, such as integrator events and peak detection thresholds, as well as data pertaining to internal and external standards for the purposes of peak identification and quantitation. The availability of these data from external sources makes a programmer's job much easier. He (or She) need only provide some rudimentary form-entry mechanism to acquire the needed data.

In the field, things may be quite different. It is appropriate to minimize the reliance of the data system on the the available personnel in order to reduce the cost of operating it. The more the data system can "figure out for itself", the more it matches the ideal case of a black box that unobtrusively provides answers rather than creating additional demands upon the available staff. Of course, the answers must be sufficiently reliable to be useful. In an attempt to address the reliance/reliability issue, a gas chromatographic software package, "M2001", has been developed at the Institute for Environmental Studies, Louisiana State University under contract with the National Oceanographic and Atmospheric Administration in cooperation with the U.S. Environmental Protection Agency. Reliance upon external data sources has been minimized while preserving the reliability of the data provided to the field staff.

Software Design.

The software described here (Figure 1) runs on Apple Macintosh computers and is designed to acquire and analyze dual-column chromatograms from a Microsensor Technologies M200 or P200 chromatograph. The main design criteria were ease of use, achieving improved peak identification by using elution patterns from both columns and minimizing operator input while maintaining credible output. This has resulted in significant improvements to the integrator, calibration system and analyzer as compared to standard chromatographic software.

The Integrator.

The integrator requires almost no operator input. It does not use integrator events, nor peak detection thresholds. The main uses of integrator events, establishing baselines and tangent skimming are handled automatically. The need for peak detection thresholds is avoided by avoiding first and second derivative tests for peak start and end detection. Although when necessary, the operator can graphically edit the integration by changing peak starts and ends, locating missed peaks and removing false peaks, the goal of the design of the integrator is to remove completely the need of such remedies.

Peak starts are located by the "Increasing Tangent" method of Woerlee and Mol¹. In this method, the start of a peak is deemed to have occurred when the tangents of the angles between a point and each of the four succeeding points increase. This method requires no threshold and therefore no operator input.

The ends of peaks are detected quite differently. A peak is deemed to have ended when a line drawn from the start of the peak merges with the chromatogram. This also requires no threshold setting and, hence, no operator input.

The scan for starts of peaks begins at the start of the chromatogram and proceeds until one has been found. After the apex of the peak has been found, both peak starts and peak ends are acceptable, allowing the start of one peak to occur on the tail of another (i.e. before the proper end of the first peak has been found).

When all the peaks have been located, it is generally the case that groups of them will share common domains (often, a common end point). Such clusters of peaks are initially treated as if they each were tangent skimmed from the immediately previous peak in the cluster. The clusters are then post-processed to locate cases of incorrect tangent skimming and to convert such cases to merged peaks.

Libraries.

The calibration and peak identification process require at least the names of the compounds that may be identified. Each compound may be thought of as having a distribution of peak pairs (one from each of the two columns) existing in a two-dimensional detection space. When both the names and the statistical descriptions of the detection space distributions of the detectable compounds are known, the detection space is said to be characterized and identification is largely a matter of matching observed peak pairs with the known distributions. The data pertaining to the distributions of the possible eluents and their names are stored in separate files called libraries.

The Calibrator.

Before further analysis can be accomplished, it is necessary to provide data on the state of the chromatograph being used. This is loosely termed "calibration" and pertains to both quantitation and qualification. Quantitative calibration consists of providing the data necessary for the program to build a function that maps peak areas into concentration or amounts. Qualitative calibration provides the program with the data necessary to calculate the expected retention time of a compound of interest under the current instrumental conditions. Although qualitative and quantitative calibration are mathematically separate operations, each requiring its own independent data and procedures, they come together at two fundamentally important places; when the operator provides the calibration, both qualitative and quantitative data will be available and when the final output is calculated, both qualitative and quantitative results will be expected. In our software, both qualitative and quantitative calibration are carried out at the same time.

Quantitative calibration is multi-point with single-point calibration supported as a special case via a calibration editor (Figure 2). From one or more previously acquired and integrated chromatograms, the operator chooses peaks with known identities and concentrations by first selecting to the name of the compound from the current library, then entering the known concentration and then pointing to the peaks that are due to that compound. This process may be repeated for as many different chromatograms or compounds as appropriate. When all the relevant peaks have been pointed out, the calibrator builds a quantitative calibration for each compound involved and a qualitative calibration for each column. It is assumed that all the calibration chromatograms represent the same instrument at the same conditions.

For quantitative calibration a regression is calculated from all the observed area/concentration pairs of each compound, the calibration function for any specific compound is simply

$$[c] = A_c + B_c \cdot \text{area}_c \quad (1)$$

where

[c] is the concentration of compound c
 A_c is the intercept of the line of regression
 B_c is the slope of the line of regression
 area_c is the area of a peak supposedly due to compound c

Qualitative calibration consists of the results of two regression analyses, one performed upon peaks from each column. Guardino's method² is used to estimate the mathematical dead time and the slope and intercept of the line of regression so that

$$I = A + B \cdot \log_{10}(T - T_m) \quad (2)$$

where

I is the retention index of a peak at retention time T
A is the intercept of the line of regression
B is the slope of the line of regression
 T_m is the mathematical dead time that minimizes r^2

This equation is rearranged to

$$T = T_m + 10^{(I-A)/B} \quad (3)$$

which is used to compute the expected retention time of every compound in the library.

The Analyzer.

The purpose of the analyzer is to compute the contents of two different sorts of windows (Figure 3). The upper window in Figure 8 is an inventory window displaying the contents of a sample. If the software and analytical procedure were totally reliable, this is the only result needed. The rest is only necessary when human intellect must be used in place of mere computation. Inventory windows contain (from left to right) the substance name, the certainty factor of the identification (1000 => a perfect match, 0 => not a match), the number of peaks upon which the identification is based, the natural log of the peak size ratio and the amount represented by the smallest peak in the identification. The lower window is one of the two peak list windows, there being one for each column. It contains the retention time, index, area, amount, and identifications of each peak detected on a column. The last three columns pertain to the identification. The column labeled "CF" contains the certainty factor of each identified component. It is possible to have a single peak result in two different identifications if there is evidence of

coelution as in the case of the peak at 11.28 seconds. The column immediately to the left the certainty factor contains the percent of the peak accounted for by the specific identification. It is the size of the peak implied by the amount given in the inventory window divided by the total size of the peak. If the percentages for a given peak add up to less than 100%, there may be an unidentifiable coeluent. It is, of course, possible for a peak to be completely unidentifiable as in the cases of the peaks at 39.52 and 43.60 seconds.

The analyzer uses a newly developed procedure to convert the identification process for peaks from multiple chromatographs to a game and, thence to a zero-one integer (mathematical) program³, the details of which are beyond the scope of this paper. Briefly, each possible combination of peaks chosen from each column together with a possible identity chosen from the library is considered an hypothesis that must be tested. Each hypothesis (Figure 4) is characterized (from left to right) by the numbers of a peak from column A, the number of a peak from column B, a certainty factor, the natural log of the peak size ratio and a possible identity. An hypothesis may be interpreted as a statement that a specific peak from column A and a specific peak from column B were both caused by the elution of a specific substance. The certainty factor and log size ratio are used to assess the validity of that statement. The analyzer accepts those hypotheses that are mutually consistent and have the largest sum of certainty factors while preferring those that involve matching similarly sized peaks (low log size ratio).

After having performed this task, it may, at the operator's discretion, analyze the accepted peak pair identifications to see if any involve matching peaks that do not have similar sizes. If this is the case, the larger peak is mathematically split into a peak that perfectly matches the smaller and a left-over peak. The identification is then recomputed taking account of the left-over peaks which allow the program to identify some cases of coeluted peaks.

Conclusion.

The authors have developed a relatively easy-to-use software package (M2001) for doing gas chromatography in the field. Unlike standard laboratory packages, M2001 requires little or no user input for integration and is capable of identifying chemical substances even when standards are hard to come by.

Acknowledgement.

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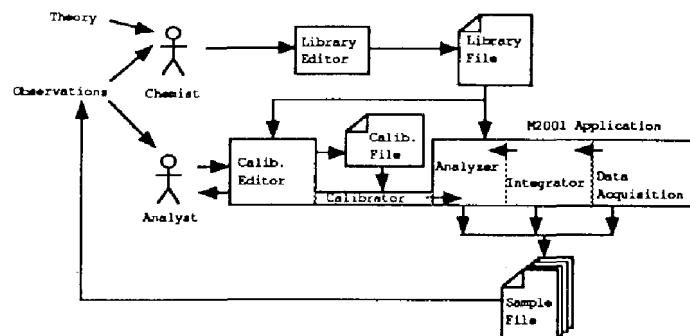


Figure 1
M2001 Application Structure

Calibrate: Cal Gas

No.	RTA	RTB	AREA(μV)
00	9.64	14296.575	
01	11.28	20449.700	
02	13.20	225.472	
03	19.36	265.560	
04	34.88	279.025	

Peak List A

No.	RTA	RTB	AREA(μV)
02	11.16	1550.420	
03	13.00	74.887	
04	21.04	87.807	
05	40.92	80.343	
06	59.72	63.177	100 octane

Peak List B

No.	RTA	RTB	Name
28	747.3	828.7	methyl isobutyl ketone
29	772.0	820.6	toluene
30	800.0	800.0	octane
31	775.5	865.8	1,1,2-trichloroethane
32	799.4	886.1	1,1,2-dibromochloroethane

LIBRARY

Concentration: 100 Units: ppm

Auto Cancel Ok

Figure 2
Calibration Editor

File Edit M200 Sample Trace Display Windows 16:29

5Min.CalGas • Inventory

Substance	CF	R	Amount
air	816	2	1
butane	825	2	4
water	995	2	1
pentane	997	2	0
hexane	998	2	0
heptane	979	2	0
octane	967	2	0

5Min.CalGas • Channel A Peaks

RT	RI	Area(μV)	Amount	CF	Substance
9.64	271	14297.25		816	air
11.28	430	21446.85	9511.96 ppm	258	995 water
13.20	500	225.47	100.00 ppm	18	825 butane
19.36	600	265.56	100.00 ppm	100%	997 pentane
34.88	700	279.02	100.00 ppm	100%	998 hexane
39.52	718	4.74	1.81 ppm		979 heptane
43.60	732	4.05	1.53 ppm		
74.04	800	261.60	100.00 ppm	100%	967 octane

Figure 3
Peak Identification Windows

24 Hypotheses (cutoff = 0)

A#	B#	CF	R	Substance
0	0	907	0	air
0	2	44	6	water
1	1	772	0	
0	1	44	6	
1	2	772	0	
3	10	351	0	methyl ethyl ketone
3	9	351	0	
3	5	129	1	hexane
3	4	129	0	
4	4	973	1	
4	5	973	0	
5	8	330	0	ethyl acetate
5	7	330	0	
6	9	241	0	chloroform
5	12	242	2	

Figure 4
Some Hypothetical Identifications

Variability in Elution Time Data from Microchip Gas Chromatographs:

Ramifications for Sample Component Identification

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The introduction of the microchip gas chromatograph in 1975 was an early application of photolithography to the construction of analytical instrumentation¹. The result was the "gc on a chip", a complete gas chromatograph on a silicon wafer the size of a microscope slide. Technical difficulties at the time, namely etching a good, symmetrical column into the silicon wafer, precluded large scale development. The technology was, however, successfully used to fabricate small injection systems and small thermal conductivity detectors. This was an excellent and timely complement to the evolving technology for production of good microbore capillary columns. The Michromonitor 500 and the newer M200 portable gas chromatographs are the descendants of these two technologies. The M200 uses micromachined injector assemblies and detectors with two 4-meter, 0.100 mm columns and thus provides the capability for chromatographic analyses of volatile organic compounds in under 2 minutes. In addition to short analysis times this combination provides for excellent short term and long term stability, evident in retention times and in detector response. The use of two columns with differing stationary phases also greatly enhances the analytical power of the system over a single column system. Clearly, the M200 has unique capabilities with respect to both qualitative and quantitative analysis.

The "M2001" software, written at Louisiana State University, takes advantage of the multidimensional nature of the information in the output of the M200. The two chromatograms are searched for peak pairs corresponding to compounds that may be in the sample. The possible compounds are distributed in a multidimensional space as points described by their retention times on each of the two columns. From the list of possible constituents the software uses an optimization procedure to select the most likely composition of the sample. The details of this identification procedure have been described elsewhere².

Theory

Of primary importance in the use of the M2001 identification procedure is the availability of a reliable database from which a list of possible constituents can be drawn. This database must contain information about the retention of each compound on each column and also information about the expected variations due to random error. This paper will focus on the generation of such a database or "library" and will discuss important sources of error and ways of avoiding them.

The quality of this database can be addressed in terms of its accuracy and precision. The accuracy of the database or "library of compounds" can be assessed by how well the values in the library predict experimentally determined retention times. The variable nature of retention times is well known and, although the M200 generally yields very reproducible retention times, the likelihood of obtaining the same retention times on different instruments or even on a single instrument over an extended length of time is small. The use of a retention index system for removing the effect of small changes in operating conditions has been used since the Kovats³ system. Thus the library of Kovats retention indices was created for a number of volatile organic compounds.. Because retention indices were known to vary, to a small degree, with time⁴ a unique second normalization step was added to the

procedure. Prior to analysis a "qualitative calibration" is performed in which the retention index library is essentially recalculated as retention times based on the retention times for a mixture of known compounds. The use of the resulting "pseudo-retention indices" for component identification is made possible by the high degree of consistency in retention times obtained with the M200.

Because the identification algorithm uses a statistically based optimization procedure, accurate estimates for the expected variability in observed retention times are important. The standard deviations given in the library for each compound will affect the statistical weight of the various mixtures proposed by the software. Incorrect standard deviations can thus lead to misidentifications by, generally, discriminating against including compounds for which the standard deviation is underestimated and in favor of including those for which the standard deviation is overestimated. It is important to note that this requirement is for accurate standard deviation estimates rather than small standard deviations *per se*. The latter is required for what might be called "qualitative resolution", the ability of the software to meaningfully distinguish between different but similar compounds. It is an instrumental requirement well met by the M200 but not what is meant here.. Accurate estimates of the standard deviation, whether large or small, are required in order to prevent systematic bias in favor of choosing particular compounds in the library.

The retention index library was based on the Kovats system, using the homologous series of n-alkanes as reference compounds. The retention index (I) for each compound was calculated on the basis of the log-linear relationship between adjusted retention time and number of carbon atoms in n-alkane molecules

$$\ln(t-t_0) = aI + b \quad (1)$$

where I=number of carbon atoms times 100, t=absolute retention time, t_0 =column dead time, and a and b are the slope and y-intercept respectively of the line. The column dead time was estimated by iterative linear regression of $\ln(t-t_0)$ on I as per Guardino *et al.*⁴ Incorrect estimates for t_0 result in curvature in the $\ln(t-t_0)$ vs. I relationship. The curve is concave upward if t_0 is underestimated and concave downward if it is overestimated. The relationship is linear only if the proper value is chosen for t_0 . Thus t_0 was adjusted to maximize the correlation coefficient for the linear regression and the values so obtained for a and b were used to calculate I for the compound of interest.

Experimental

Headspace vapors of 35 compounds were individually mixed with nitrogen containing 100 ppm each of butane, pentane, hexane, heptane and octane. Concentrations of the 35 compounds were kept between 100 and 1000 ppm to prevent column overloading. Compounds that eluted near one of the n-alkanes were diluted with ambient air rather than the alkane mixture to avoid interference from unresolved peaks. Samples were initially run at column temperatures of 60°C using mean carrier gas velocities of 45 to 50 cm/sec (0.21 to 0.23 ml/minute). Zero grade helium was used as the carrier gas throughout. Each of the 35 compounds was run in duplicate. Approximately 3 days were required to complete the 35 samples. After an approximately 7 day interim, the 35 compounds were again analyzed in duplicate over a three day period. The analysis sequence was scrambled to reduce the effect of possible time dependent

changes. The entire analysis was repeated a third time again after a 7 day interval. Thus three sets of data were available for calculating retention indices at 60°C.

After obtaining the 60° retention data, the process was repeated at temperatures of 80°, 50°, 40°, and 70°. The column head pressure was not changed so the analyses were actually performed with slightly different carrier gas flows due to the temperature dependence of the carrier gas viscosity. This amounted to a variation of about 5% between the flow at 40° and that at 80°. Each compound was again run in duplicate but the entire sequence of compounds was only performed once at each of these other temperatures.

Results

The retention times of the n-alkanes proved to be highly reproducible. The sequence chart in Figure 1 shows both the short term variability in the retention times as well as their general stability over a period of several weeks. The relative standard deviations of the alkane retention times were well under 0.5% over the course of each three day period. Furthermore, the retention times showed no significant difference between three day periods if the instrument was left running. The 7 day periods separating each three day series are represented by solid vertical rules in Figure 1. The instrument was shut down and the gas flow was turned off for several days between the first and second series but the column temperature gas flow was maintained during the week between the second and third series. The retention times show a considerable change between the first and second series while those in the second and third series are essentially the same. The important feature here is that if the conditions are unchanged then the retention times are remarkably stable.

Because of the highly stable nature of the alkane retention times, the linear regression estimate of equation (1) could be obtained using the average retention time of each alkane over the approximately 70 runs in the relevant three day period. This method had two advantages. First, the confidence intervals for the average alkane retention times were much smaller; they provided an order of magnitude improvement in precision over a single observed value. Secondly, by using the average values for the entire series as reference retention times retention indices for all compounds are calculated on the same basis rather than using internal references for some compounds and external references for those that coelute with one of the n-alkanes. A small portion of the library calculated on the basis of the retention times in Figure 1 is shown in Table I. They correspond to the first, second and third series in Figure 1. The important feature to note here is that the retention times are reproduced very well even though there is a definite shift in absolute retention times between the first and second series.

Regardless of its stability with time, the library is of limited use if it is not transportable to different instruments. As an initial test of library portability, some library compounds were run on new M200 columns. The library was created on an instrument that has been in continuous service for approximately 18 months. The carrier flow on the new columns was adjusted to that at which the library was originally created and a sequence of n-alkanes was analyzed at 4 temperatures. The results are summarized in Tables II and III by the deviations from a reference chromatogram obtained at the same time on the M200 used to create the library. Also included are results from a chromatogram obtained 8 weeks previously which had actually been used in creating the original library. It appears from the average deviations, shown in Table II, that one must lower the temperature to 59° in order to

reproduce the results from the reference M200. Looking at the deviations in terms of per cent deviation (Table III), a different conclusion may be drawn. While the 58° result still provides the lowest total deviation, the 60° result provides an essentially constant relative deviation from the reference chromatogram. Upon the logarithmic transformation used in both the retention index calculations, relative errors are transformed into absolute errors. Thus a constant relative error of 5% becomes a constant absolute error of 0.05 in the logarithmic data. This is exactly the type of error that is well treated by retention index comparison. In other words, even though the 58° result appears to more closely match the reference data in terms of absolute deviations, the deviations in the 60° data will be essentially eliminated as a constant offset value in the logarithmically based library. This is demonstrated by the summary in Table IV. The nominal results are those in which the new M200 columns were set at the same flow rate and temperature as the reference M200 (i.e. 60°C). The tuned results were obtained by adjusting the column conditions until the n-alkane retention times most closely approximated those obtained with the reference instrument (i.e. 58°C). This is somewhat like physical creating a retention index system. These results parallel those for the n-alkanes above; while the retention times were forced into a much better agreement by adjusting the column conditions, deviations were adequately handled by the mathematical retention index system.

Ideally one should be able to use this retention index library without regard to temperature. Unfortunately, the temperature dependence of Kovats retention indices is well known and may, in fact, contain some useful qualitative information. The results from the several temperatures at which the compounds were run clearly show a correlation between temperature calculated retention index. For most compounds in this library, the variation was less than 8 retention index units for a 40° swing in temperature. This can be a significant problem for early eluters for which a change of 8 retention index units can correspond to quite a large difference in the retention predicted by the software. For later eluters the problem may be less significant. Furthermore, the nature of the correlation between I and temperature is clearly structure related; all compounds which showed a negative correlation were oxygen containing compounds such as ketones, esters and alcohols. All other compounds, including those with some polarity (e.g. chloroform and ethyl bromide) as well as nonpolar compounds and aromatics exhibited negative correlations. While the extent of these variations has not been well characterized at present it seems likely that one would be able, under some circumstances, to use the library at temperatures other than that at which it was created, albeit with a loss of reliability in the resulting identifications. If, however, the general class of compounds one expects to find in the sample are known (e.g. halocarbons), then using compounds of that class as standards in the qualitative calibration would allow use of the library over a range of temperatures without such a loss in reliability for those compounds. Reliability for compounds not in that class would, of course be severely compromised.

Summary

A retention index library containing a number of volatile organic compounds has been created for use with a statistically based identification algorithm. The high reproducibility of retention times obtained from the M200 allows the use of external retention index standards. These external standards can be used to "calibrate" the library thus allowing the library to be used with slightly different

column conditions or with different M200 instruments. This calibration creates "pseudo-retention indices" based on observed retention times of the standards and entries contained in the main retention index library presented here. The standards need not be, and occasionally should not be, the normal alkanes required under the true Kovats system. An observed temperature dependence limits the use of this particular library to temperatures quite near 60°. Given the fact that many compounds show similar types of correlation between I and temperature, the usable temperature range may be increased for a similar class of compounds by using members of that class as qualitative standards.

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OV-73 column at 60°C

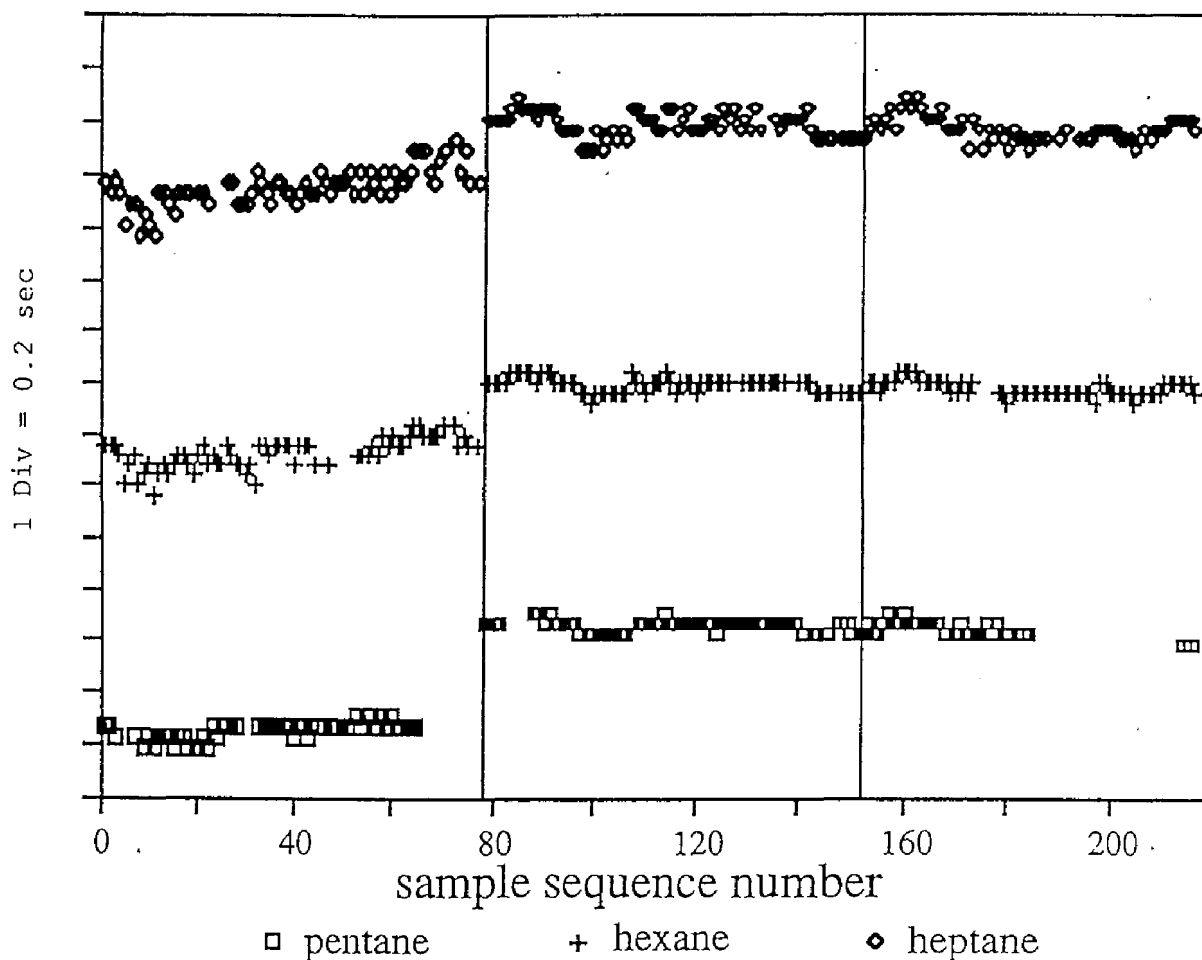


Figure 1. Sequence chart for n-alkane retention times. Vertical rules indicate 1 week interval between samples.

TABLE I
Retention indices determined at 1 week intervals

Compound	Index #1	Index #2	Index #3	s.d.
vinyl acetate	586.6	585.6	585.3	0.75
hexane	600.9	600.0	599.8	0.67
methylethyl ketone	604.7	604.7	604.4	0.19
ethyl acetate	620.6	620.1	620.2	0.30
chloroform	623.7	623.7	623.7	0.03
benzene	669.6	669.3	669.4	0.14
cyclohexane	669.4	669.8	669.7	0.21
carbon tetrachloride	669.8	669.8	670.1	0.19

TABLE II
Absolute deviation (seconds) from reference M200 retention times

	Reference M200				
	8 weeks				
	previous	60°	59°	58°	55°
n-pentane	0.15	-0.52	-0.44	-0.32	-0.04
n-hexane	0.15	-0.88	-0.60	-0.24	0.68
n-heptane	0.13	-1.45	-0.65	0.31	3.03
n-octane	0.04	-2.24	-0.08	2.56	9.96
AVERAGE	0.116	-1.272	-0.442	0.578	3.408

TABLE III
Per cent relative deviation from reference M200 retention times

	Reference M200				
	8 weeks				
	previous	60°	59°	58°	55°
n-pentane	1.08	-4.06	-3.42	-2.46	-0.30
n-hexane	0.75	-4.62	-3.11	-1.22	3.30
n-heptane	0.37	-4.32	-1.89	0.88	7.96
n-octane	0.06	-3.33	-0.12	3.55	12.52
AVERAGE	0.56	-4.08	-2.13	0.19	5.87

TABLE IV
Relative standard deviations between instruments

Substance	Retention Time		Retention Index	
	Nominal	Tuned	Nominal	Tuned
Acetone	6.70	0.90	0.17	0.13
Methylethylketone	7.17	0.64	0.14	0.02
Dichlorobromomethane	8.85	0.07	0.04	0.07
Dibromochloromethane	8.17	0.14	0.05	0.05

A FRACTIONAL (FRACTAL) BROWNIAN MOTION MODEL
OF ATMOSPHERIC DIFFUSION

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Present atmospheric diffusion models assume, directly or implicitly, that atmospheric turbulence motions are of the classical Brownian type. A nineteen-month series of 12-hour averaged values of Kr^{85} concentrations measured at Murray Hill, NJ, 1050 km downwind from the source near Aiken SC has been analyzed using a method of fractal geometry, the R/S (renormalized-range) statistic. The result achieves a high degree of organization of the initially extremely variable time-series of observed air concentration values. The slope of the R/S curve indicates that large-scale atmospheric diffusion is controlled by large-scale, random air motions that are qualitatively different from the usual assumption of Brownian motion. Real atmospheric motions at large scales are richer in high-frequency components than their Brownian counterpart, and exhibit correlation at all scales. The fractal nature of this scale of turbulent atmospheric motions, and a computer algorithm for generating the appropriate fractal Brownian motion for use in diffusion models, are briefly discussed.

INTRODUCTION

In very general terms, turbulent tropospheric motions appear to be a mixture of two rather distinct kinds: large, quasi-horizontal, essentially two-dimensional motions of scales greater than several hundred kilometers; and smaller, three-dimensional eddy motions. The former cascade eddy enstrophy (mean-squared random vorticity) from the very large scales of eddy kinetic-energy generation (several thousand km) to scales of a few hundred km. The latter dissipate this random vorticity by rapidly attenuating, distorting and concentrating it and cascading the eddy kinetic energy to the very small (<1 cm) scale of viscous dissipation (Gifford¹¹). This view of the nature of atmospheric turbulence is supported by the extensive measurements of eddy-energy spectra reported by Nastrom and Gage¹⁹ and by the atmospheric diffusion data summarized by Gifford^{7,8} and Barr and Gifford².

A cloud or plume of contaminant material diffusing in such a field of random eddies is in effect sampling the turbulence structure through an ever-increasing volume of the atmosphere. At first, in the energy-cascade region, spreading is rapid because, as was pointed out by Batchelor³, the range of eddy sizes present always includes those that are just the size of the plume. Later, after many hours of downwind travel, the cloud expands into the enstrophy-cascade range of eddy sizes. This range (Gifford *et al.*¹², Gifford¹¹) is characterized by rapid cloud distortion due to the large eddies, accompanied by diffusion at a slower rate. Large clouds quickly develop very irregular outlines, as shown by the long volcano plumes studied by Gifford¹³ and the evolution of the Chernobyl plume discussed by Smith²⁰. Although it has so far always been ignored in (short-range) studies of atmospheric diffusion of clouds and plumes, the large outer time-scale of turbulence, about 10^4 sec, implied by this two-range view of atmospheric turbulence structure (Gifford^{9,11,12}) has been shown also to influence diffusion at smaller scales (Gifford¹⁰).

FRactal Dimension of Pollutant Clouds

The observed shapes of energy spectra in the earth's troposphere, especially the extensive GASP spectra¹⁹, strongly suggest a large-scale, enstrophy-cascade range and a smaller-scale, energy-cascade range of turbulent atmospheric motions. The eddy dynamics of each range are governed, respectively, by random enstrophy and energy transfer and can be assumed to be quantitatively described solely in terms of the corresponding similarity parameters (Gifford¹¹). It follows that passive scalar functions of the turbulence, such as pollutant concentration, will exhibit self similarity. That is, changes in concentration must depend on time in such a way that in a statistical sense, for any two times t_1 and t_2 ,

$$C(t_2) - C(t_1) \propto (t_2 - t_1)^H \quad (1)$$

The similarity constant H , known as the Hurst exponent, is in the case of a time series related to the fractal dimension, D , by

$$D = 2 - H \quad (2)$$

The idea of fractal dimension was introduced by Mandelbrot¹⁶ to account for the fact that natural shapes, including cloud outlines and turbulence among many other atmospheric phenomena, are not measured by the Euclidean metric that applies to smooth, regular, geometrical objects. The fractal dimension, which exceeds the Euclidean dimension (and is usually fractional) is in effect an index of an object's irregularity. Lovejoy¹⁷ showed that

the fractal dimension, D , of the perimeters of clouds and rainbands and by inference of atmospheric turbulent eddies, equals 1.35 over a broad range of eddy scales. Gifford¹³ showed that this applies up to linear scales of about 300-400 km, or time scales of a few times 10^4 seconds, but that at larger scales, in the enstrophy-cascade region, $D \approx 1.8$, indicating turbulence of a markedly different type.

Squaring equation (1) and averaging gives the variance

$$\langle \delta C^2 \rangle \propto \delta t^{2H} \quad ; \quad (3)$$

δC is the concentration increment over the time lag, $\delta t = t_2 - t_1$. Also from Eq.(1), the so-called "renormalized-range" statistic (Mandelbrot¹⁸) can be written as

$$[C_{\max}(\tau) - C_{\min}(\tau)]/\sigma_C(\tau) = R(\tau)/S(\tau) = b\tau^H, \quad (4)$$

where R is the range and S ($=\sigma_C$) is the standard deviation of C during the time interval $\tau = t_1 - t_0$. The slopes of logarithmic plots of either $\langle \delta C^2 \rangle^{1/2}$ vs. δt , or of R/S vs. τ should contain broad, linear ranges if atmospheric turbulent motions are self-similar. Atmospheric values of the similarity exponent H , and of the fractal dimension D of atmospheric turbulence, follow directly from these slopes.

FRACTIONAL BROWNIAN MOTION IN ATMOSPHERIC DIFFUSION MODELING

All atmospheric diffusion models assume that turbulence can be simulated by Brownian motion. This is done either directly, as in models of the Lagrangian particle motion (e.g. Hanna¹⁴; Gifford⁶) or indirectly, through the assumption of Gaussian turbulence statistics in plume models or by the use of K-theory. The turbulent velocity $v(t)$, and consequently the position of a pollutant particle, can be expressed as

$$v(t+\delta t) = v(t) + r(t) \quad (5)$$

(Hanna¹⁴), where $r(t)$ is a random velocity with Gaussian statistics; $r(t)$ is the integral of a random acceleration, $a(t)$, which has Brownian motion (white noise) statistics,

$$r(t) = \int_{-\infty}^t a(x) dx \quad . \quad (6)$$

The quantity r is called the trace of the Brownian motion process, a . Such a Gaussian random process has the well-known properties, $\langle r(t) - r(t_0) \rangle = 0$, and

$$\langle [r(t) - r(t_0)]^2 \rangle (= \sigma_r^2) \propto t \quad , \quad (7)$$

where $\langle \dots \rangle$ represents ensemble averaging.

Mandelbrot¹⁸ proposed the following generalization of the classical Brownian motion model;

$$\langle [r(t) - r(t_0)]^2 \rangle \propto t^{2H} \quad , \quad (8)$$

where $0 < H < 1$. From Eq.(7), H is equal to $1/2$ for ordinary Brownian motion. In nature H is not usually equal to $1/2$; natural noise signals are not ordi-

narly white. By fitting various kinds of long, natural time-series (river discharges, tree ring data, varves, etc.) to Eq.(4), it has been found (Feder⁵) that often $H \approx 0.7-0.8$. The assumption that atmospheric turbulence is of the Brownian motion type, implying that $H = 1/2$, is known to result in fairly good estimates of atmospheric diffusion (cf. Gifford⁶, for example) which is, of course, why it is a staple of diffusion modeling. Yet systematic departures are known to occur and should be of concern to modelers. Theoretical arguments, for instance by Hentschel and Procaccia¹⁶, in terms of fractal geometry for the case of fully-developed homogeneous turbulence indicate that H should be about $1/3$.

Fractal Brownian motion (fBm) curves for various values of H are qualitatively quite different in shape. For H -values of $0.7-0.8$, corresponding to the river-discharge, varve, and tree-ring data, high-frequency spikes are small and the fBm curve is relatively smooth. For $H=1/2$, the white-noise of ordinary Brownian motion, all frequencies are equally represented and the curve is uniformly rough. For small values of H , closest to the case of atmospheric turbulence, the fBm curve is decidedly rougher at all scales.

The physical meaning of H is perhaps most readily conveyed by relating fBm to the more familiar power-spectrum representation. In a similarity region of the spectrum, the slope is equal to $1/f^\beta$, f being frequency. The fractal dimension of the spectrum equals (Mandelbrot¹⁸)

$$D = E + 1 - H = E + (3-\beta)/2 \quad (9)$$

where E is the spectrum's Euclidean dimension. For time spectra $E=1$ and $D=2-H$. Since $0 < H < 1$, the following values are found:

$H:$	0	1/3	1/2	1
$\beta:$	1	5/3	2	3
$D:$	2	5/3	3/2	1

$H=1/3$ is the theoretical value for a Kolmogoroff fBm, i. e. an inertial-range spectrum. $H=1/2$ gives the well known $1/f^2$ spectrum of the trace of ordinary Brownian motion. The character of the autocorrelation curve is also governed by H . For $H=1/2$ the fBm is uncorrelated; the future is completely independent of the past. For $H > 1/2$ the fBm exhibits persistence; departures from the mean tend to be followed by even larger departures. In the limit of large time, the correlation remains positive. For $H < 1/2$ the limiting value of the correlation is negative, indicating antipersistence; large departures tend to be followed by a return toward the central value.

Until the development of fractal geometry there has been no way to take such subtle and pervasive differences in the detailed shapes of turbulence functions into account in models and, indeed, little by way of a quantitative perception of their existence. Clearly it is desirable, at the very least, to undertake studies to find out how H behaves in the atmosphere and how to include it in diffusion models. The following example illustrates something of what can be done along this line.

ANALYSIS OF CONCENTRATION-TIME SERIES

Heffter¹⁵, et al., monitored Kr^{85} concentrations at five sites northeast of the Savannah River plant in Aiken, SC, the most distant (1058 km) being that at Murray Hill, NJ. Twelve-hour averaged values of ground-level Kr^{85} concentration were recorded for a period of 19 months. Figure 1, a plot of the Murray Hill data, illustrates their extreme variability.

Values of the statistic R/S , Eq.(4), were calculated for time intervals ranging from 30 to 1158 half-days from the start of measurement. The resulting curve, Figure 2 (open circles), is quite interesting; it contains three, roughly linear segments, each having about the same slope but separated from its neighbor by a sharp jump in R/S . Inspection of the concentration observations shows this to be due to the presence of two sharp spikes in the Murray Hill data; these may have been caused by Kr^{85} from the Oyster Creek (NJ) reactor, the only nearby source capable of producing such features. The two spikes were removed by a linear interpolation between adjacent concentration points, a minor adjustment of 4 data values. The resulting modification to the R/S values is shown as the dotted curve (2) in Fig.2. The extraordinarily high degree of organization produced by this simple transformation of the initially random data of Fig.1 has no parallel in the writer's experience of atmospheric turbulence data and argues strongly for the fractal nature of atmospheric turbulence at these large (>300-400km) scales.

A straight line fitted to the log-log plot of the adjusted R/S -curve points produces the value $H=0.36$, corresponding to the fractal dimension $D=1.64$. It is much too early to draw final conclusions about the general significance of this value, except that it certainly agrees with both the theoretical results by Hentschel and Procaccia¹⁶ for the fractal dimension of large-scale relative diffusion, and with the observed value for aqueous clouds spreading in the enstrophy-cascade range found by Gifford¹³. It appears, from the result, that atmospheric turbulence is not in general characterized by $H=1/2$, as usually assumed. At least at larger scales it has an H -value on the order of $1/3$. Fortunately, the methodology for introducing fBm with proper H -values already exists, having been developed in connection with the seemingly unrelated problem of the video-simulation of natural landscapes and clouds (Mandelbrot¹⁸; see also Feder⁵ and Barnsley *et al.*¹). Computer algorithms for generating the fBm curves discussed in the last two references are based on the following generalization of Eq.(6),

$$r(t) \approx [1/r(H + 1/2)] \int_{-\infty}^t (t - t')^{H-1/2} dr(t'), \quad (10)$$

which is seen to reduce to (6) when $H=1/2$.

CONCLUSION

The possibility of introducing realistic fBm into atmospheric diffusion models is one of the most attractive applications of the fractal geometry methodology and distinguishes it sharply from the usual similarity theory of turbulence spectra, to which it is related by Eq.(9). Verifying that $H \approx 1/3$ for large-scale motions, and finding its value at other atmospheric scales, are urgent research goals. This approach has the potential to free diffusion modelers from the need to make an assumption about the nature of atmospheric turbulence that now appears to be unrealistic.

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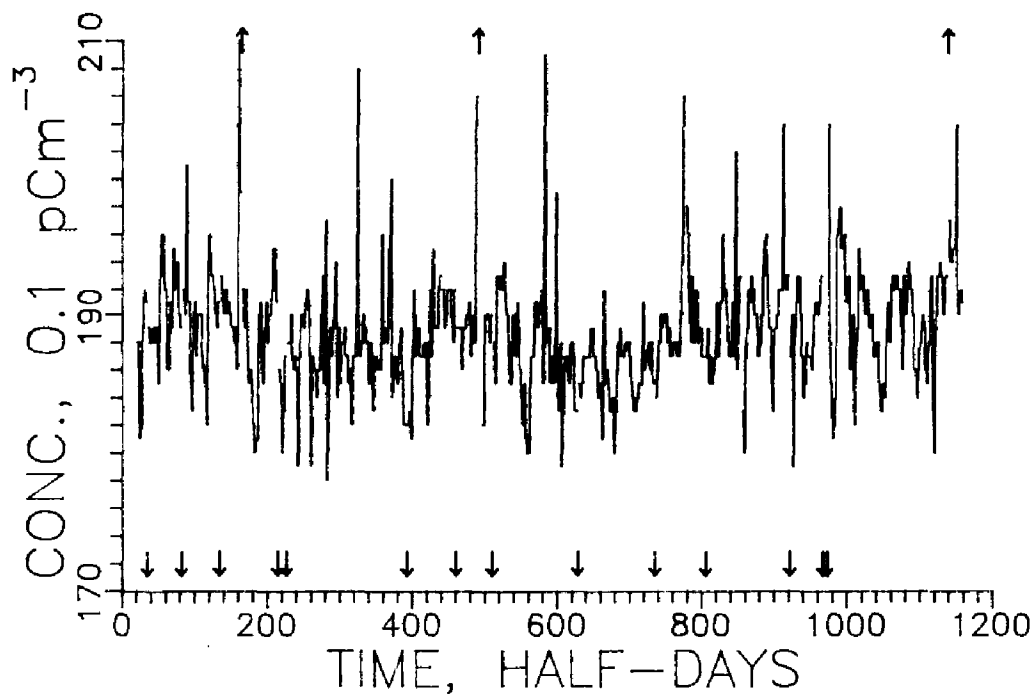


Figure 1 Successive 12-hour average values of Kr^{85} air concentrations measured at Murray Hill, NJ, for 19 months beginning March, 1982. Down-arrows indicate zeros and up-arrows indicate points above 25 pC/m^3 .

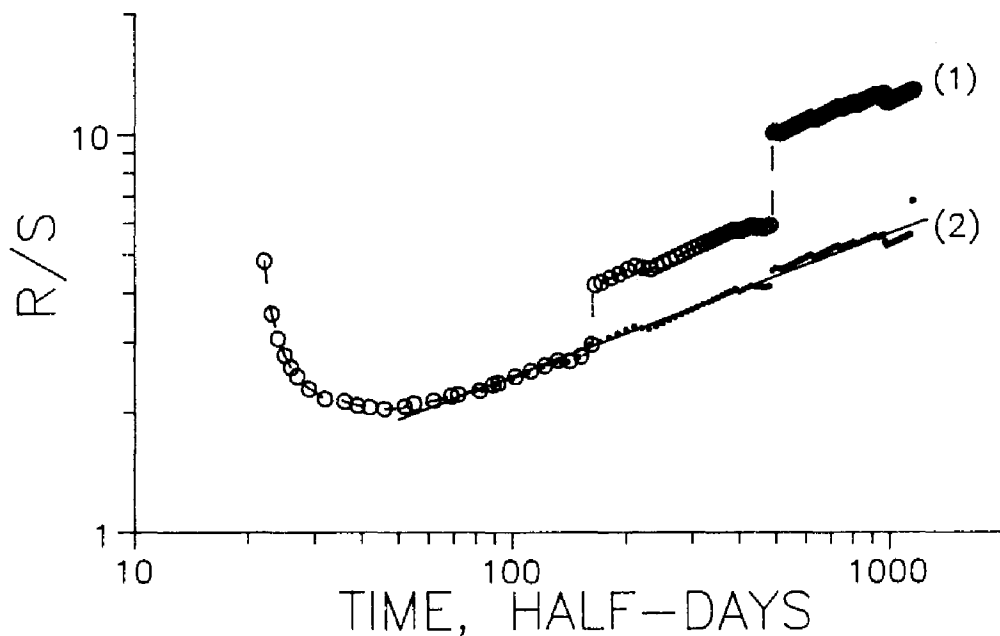


Figure 2 Renormalized range, R/S , vs. time interval, r , for Murray Hill Kr^{85} data, based on Eq.(4). Open circles, curve (1), are based on the 1158 unmodified data points of Fig.1. Small, solid dots, curve (2), show the effect of smoothing the two highest data peaks (4 data points).

Numerical Simulations of the Mountain Iron Tracer Data

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Extensive field experiments were conducted during 1965 and 1966 near Vandenberg Air Force Base. The experiments included wind speed and wind direction measurements at several towers, upper air soundings by radiosondes, and fluorescent particle releases to characterize the diffusion processes.

The data provide a unique opportunity to test numerical models under realistic boundary conditions: land-sea contrast and complex topography. We used HOTMAC (High Order Turbulence Model for Air Circulations), a three-dimensional mesoscale model based on simplified turbulence-closure equations to simulate temporal and spatial variations of wind, temperature, mixing ratio of water vapor, and turbulence distributions.

Surface concentrations were computed by using a three-dimensional transport and diffusion model RAPTAD (Random Puff Transport and Diffusion). RAPTAD is a Lagrangian puff code based on the Monte Carlo statistical diffusion process. The center location and standard deviation of concentration distribution for each puff are computed by using wind and turbulence modeled by HOTMAC. Then, the concentration at any location is computed by summing concentrations contributed by all the puffs.

Introduction

The purpose of this study is to simulate the transport and dispersion of atmospheric pollutants in the complex terrain surroundings at Vandenberg Air Force Base (VAFB) by using the Los Alamos National Laboratory (LANL) atmospheric models HOTMAC and RAPTAD.¹

HOTMAC is a prognostic model and solves a set of time-dependent physical equations such as conservation equations of momentum, internal energy, and mixing ratio of water vapor. Prognostic models can forecast three-dimensional distributions of wind speed, wind direction, temperature, mixing ratio of water vapor, and turbulence variables.

HOTMAC provides RAPTAD both mean and turbulence variables to simulate transport and diffusion processes of airborne materials. Only a few mesoscale atmospheric models can forecast three-dimensional variations of atmospheric turbulence. Therefore, HOTMAC and RAPTAD offer a considerable improvement over the current emergency response management models at VAFB that are extremely simple.

The Mountain Iron Diffusion Experiments

The Mountain Iron (MI) diffusion experiments² were conducted at VAFB during 1965 and 1966 to establish quantitative diffusion predictions for use as range safety tools in the "South Vandenberg" (SV) ballistic and space vehicle operations.

The experimental site, SV, is located along the California coast approximately 160 km west-northwest of Los Angeles. The coastline is oriented in approximately a north-south direction along the western side of SV, but changes abruptly at Point Arguello to an east-west direction. The coastline gradually changes to a north-south direction down to Point Conception and then changes again to an east-west direction. The Santa Ynez Mountains form an east-west barrier along the coastline far south of SV.

Fluorescent pigment zinc sulfide particles with a geometric mean of 2.5 microns in diameter were released to understand transport and diffusion processes and derive an empirical formula for the pollutant concentration distribution in the SV area. The effective release height was 2 to 6 meters above ground. The primary sampler used was a membrane filter inserted in a disposable polyethylene holder. The bulk samples from the field were assayed by use of the Rankin counter, which uses an alpha emitter to activate the fluorescent pigment deposited on the membrane filter.³

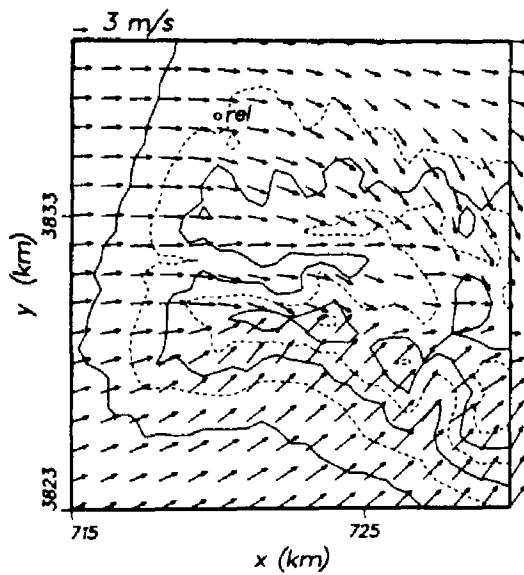


Figure 1. Modeled horizontal wind vectors at 6m above the ground at 1300 lst, June 13, 1966. Terrain is contoured by solid lines with an increment of 200 m. Dashed lines indicate contours halfway between the solid contours.

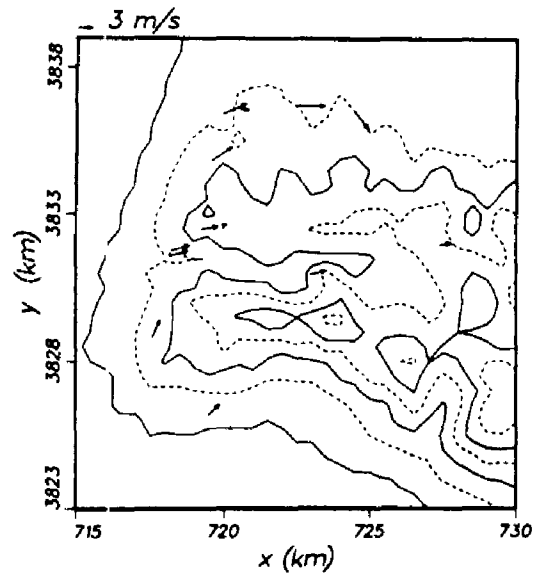


Figure 2. Same as in Figure 1 except observed wind vectors in the surface layer are shown.

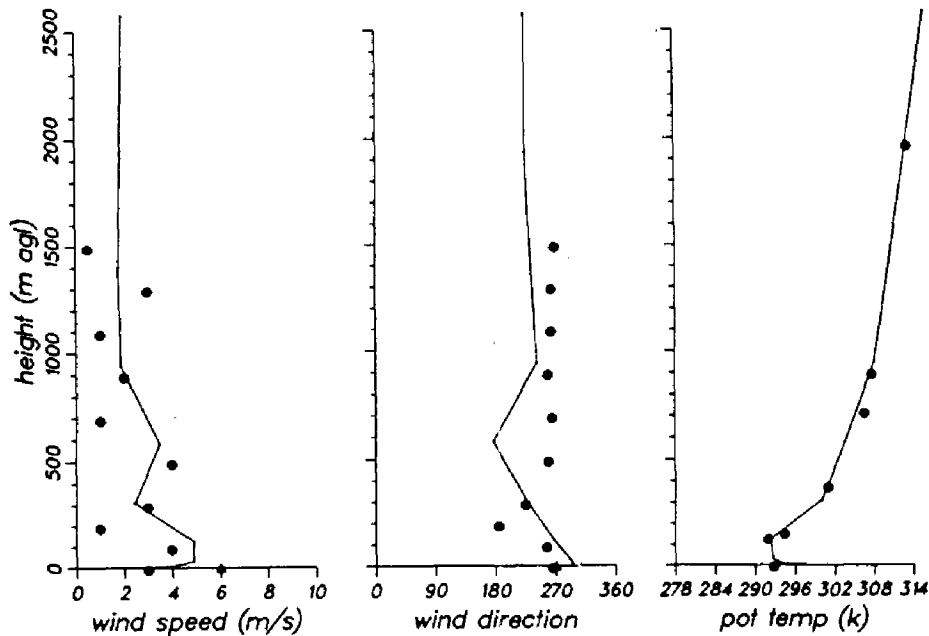


Figure 3. Vertical profiles of the modeled wind speed, direction, and potential temperature at 1300 lst, June 13, 1966 at B22. Solid circles indicate observations.

Results and Discussions

A total of 113 tracer releases was made from which we selected the MI87, MI90 and MI91 cases to evaluate the performance of HOTMAC and RAPTAD. Only the results from the MI87 simulations are reported here.

The initial potential temperature profile was determined by averaging the four upper air soundings at 1300 local standard time (lst) in SV. The potential temperature lapse rate was approximately 0.044° C/m from the sea surface to 460 m mean sea level (msl), $0.0142^{\circ}\text{ C/m}$ between 460 m and 960 m, and $0.0045^{\circ}\text{ C/m}$ above 960 m msl. Wind speed and direction were determined by examining five upper air soundings (four locations mentioned above plus VIP-1) at 1300 lst. Initial upper air wind speed and wind direction were estimated to be 2 m/s and 225 degrees, respectively.

The computational domain is $40 \times 48\text{ km}^2$ with a horizontal grid spacing of 1 km. To resolve the details of topography in the vicinity of the release site, we decided to nest a fine resolution grid $15 \times 16\text{ km}^2$ with horizontal grid spacing of 0.5 km.

Integration started at 0500 lst, June 13, 1966 and continued for over 12 hours. The plume was released at 1310 lst for 30 minutes as was done in the experiment. The plume was followed for 4 hours in the model computation. By that time the plume was transported far away from the sampling areas.

Figure 1 shows the modeled horizontal wind vectors in the inner computational grid at 6 m above the ground at 1300 lst, June 13 (Julian day 164). Although the upper air wind direction is 225 degrees (southwest), upslope flows develop in the surface layer due to heating at the sloped surfaces.

The modeled wind distribution (Figure 1) is in good agreement with the observation (Figure 2). The observed winds show much more variations in space than the modeled winds. Observations adjacent to each other show considerable variations in direction and magnitude. On the other hand, the modeled wind field varies more slowly in space than the observed since the model neglects subgrid scale variations of the surface (the grid resolution is 500 m). Nevertheless the simulation successfully reproduced many features observed.

Less satisfactory results are obtained in comparison of the vertical profiles of the modeled wind speed and wind direction with observations (Figure 3). Wind speed and wind direction become highly variable in space and time when the prevailing wind speed is small. It is noted that the observations were instantaneous values whereas the modeled results are ensemble averages. On the other hand, potential temperature is relatively stationary unless synoptic scale disturbance such as fronts pass through the measurement area.

Significant changes in the modeled wind direction occurred at around 600 m above the ground. This is caused by the mass conservation constraint to compensate the divergence and convergence of the wind distributions in the boundary layer

(Figure 3). Observed wind direction profiles appear to support such variations but the changes appear to occur at heights much closer to the ground than those modeled.

Figure 4 shows the modeled ground level concentration contours and Figure 5 shows the corresponding observation. Figure 5 also shows the observed wind speeds and wind directions at the ground stations. The observed wind direction close to the release site is west-southwesterly, but changes to westerly at the station slightly north of the release site. Our simulation (Figure 1) indicates that the wind direction is close to westerly at the release site. The observed plume apparently transported to the east-northeast direction despite the fact that wind directions measured at the ground stations suggest the plume should be transported to the east-southeast which is the case for the modeled plume.

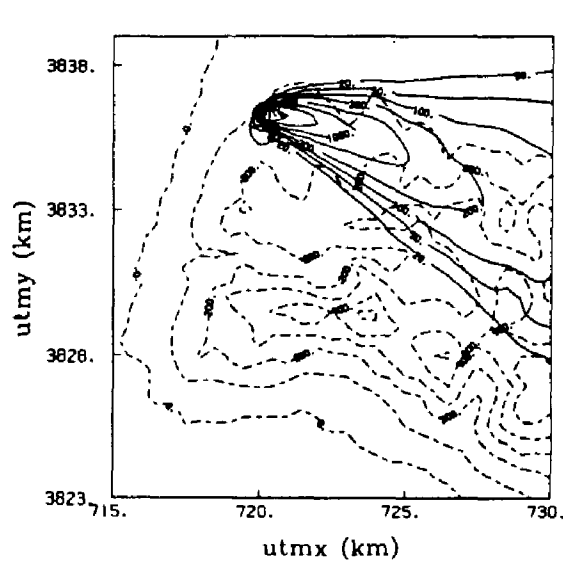


Figure 4. Modeled ground level concentration (accumulated).

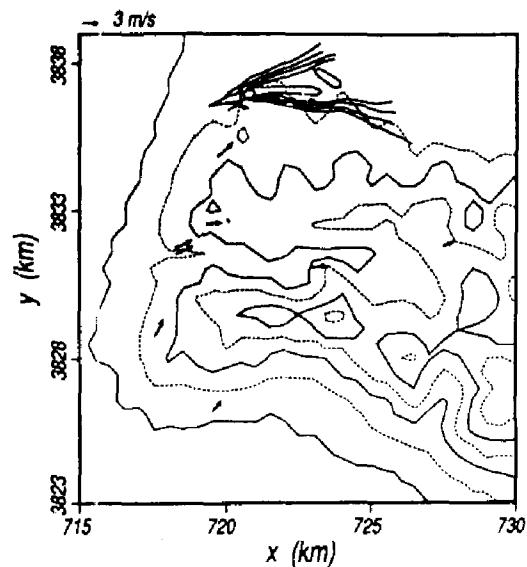


Figure 5. Observed ground level concentration (accumulated).

Although the modeled plume direction did not match the observed one, the modeled ground level concentration along the plume axis are in good agreement with observations as shown in Table I. It is not known why the observation at 3310 m from the source shows the largest value among the observations.

Table I: Normalized Concentrations

Modeled		Observed	
Distance from the source (m)	Concentration	Distances from the Source (m)	Concentration
716	8.04×10^{-6}	720	3.97×10^{-6}
1253	2.55×10^{-6}	1260	1.08×10^{-6}
3312	9.06×10^{-7}	3310	5.39×10^{-6}
4403	7.08×10^{-7}	4400	3.02×10^{-7}

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THE INCLUSION OF POLLUTANT REMOVAL PROCESSES IN URBAN AIR QUALITY MODELS

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Gaseous and particulate pollutants emitted into the atmosphere are removed by several natural processes. Important among them are the dry deposition of pollutants at the earth's surface, and chemical transformation in the atmosphere. These removal mechanisms affect the pollutant concentrations and residence times in the atmosphere and, therefore, it is necessary to account for them in air quality models. This is particularly important for urban air quality models, which are often used to assess the risk associated with chronic exposure of population to toxic air contaminants.

This paper describes a methodology for including dry deposition and a first-order chemical transformation in urban air pollution models based on the Gaussian-diffusion framework. The concentration algorithms for point sources are derived from analytical solutions of a gradient-transfer model. In the limit, when deposition and settling velocities and the chemical transformation rate are zero, these expressions for various stability and mixing conditions reduce to the familiar Gaussian plume diffusion algorithms without the removal processes. The point-source algorithms are integrated to obtain the concentrations due to emissions from distributed urban area sources. A new mathematical approach, based on mass budget considerations, is outlined to derive simple expressions for ground-level concentrations. The concentration and deposition flux formulations described in this paper are currently used in several of EPA's air quality models.

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Introduction

Pollutant gases and particles released into the atmosphere are transported by the wind, diffused and diluted by turbulence, and removed by several natural processes. Among the important removal mechanisms are chemical transformation in the atmosphere, and dry deposition of pollutants at the earth's surface by gravitational settling, turbulent transfer, chemical adsorption, and other effects. Depletion of airborne pollutant material by these physical processes affects its concentrations and residence times in the atmosphere. Surface deposition of pollutants may adversely impact on human health, local ecology, structures, and monuments. It is necessary, therefore, to consider the removal processes in air quality models in order to obtain reliable estimates of the concentrations and surface deposition fluxes.

This paper describes a methodology for incorporating the dry deposition and first-order chemical transformation of gaseous or particulate pollutants in urban air pollution models based on Gaussian plume-diffusion assumptions. The concentration algorithms are derived from analytical solutions of a gradient-transfer model^{1,2}.

Model Formulations

We consider the steady state form of the three-dimensional atmospheric advection-diffusion equation (see Rao²) for the concentration C of the pollutant:

$$U \partial C / \partial x = K_y \partial^2 C / \partial y^2 + K_z \partial^2 C / \partial z^2 + W \partial C / \partial z - C / \tau_c \quad (1a)$$

Here, x, y , and z are the horizontal downwind, crosswind, and vertical coordinates, respectively; U is the constant average wind speed, K_y and K_z are the eddy diffusivity coefficients, W is the gravitational settling velocity of the pollutant, and $\tau_c \equiv 1/k_t$ is the time scale associated with the chemical transformation which proceeds at a known rate k_t . For a continuous point source, which emits pollutant at a rate Q from $(x = 0, y = 0, z = H)$, the initial and boundary conditions are given by

$$C(0, y, z) = Q/U \cdot \delta(y) \cdot \delta(z - H) \quad (1b)$$

$$C(x, \pm\infty, z) = 0 \quad (1c)$$

$$[K_z \partial C / \partial z + W C] = [V_d C] \quad \text{at } z = 0 \quad (1d)$$

$$C(x, y, \infty) = 0 \quad (1e)$$

where δ is the Dirac delta function. Equation 1d states that, at ground-level, the sum of the turbulent flux of pollutant and its downward settling flux due to the particles' weight is equal to the net flux of pollutant to the ground, resulting from an exchange between the atmosphere and the surface. The deposition velocity V_d characterizes this exchange. When deposition occurs, the turbulent flux of the pollutant at the surface ($z = 0$) is given, from Equation 1d, by $-\overline{w'c} = K_z \partial C / \partial z = (V_d - W) C \geq 0$ which implies that $V_d \geq W \geq 0$. The deposition boundary condition (Equation 1d), suggested by Monin² and Calder³, was discussed by Rao¹.

The exact analytical solution of Equation 1 can be written (see Rao^{1,2}) as

$$C(x, y, z) = Q/U \cdot g_1(x, y)/L_y \cdot g'_2(x, z)/L_z \quad (2)$$

where g_1 and g'_2 are nondimensional functions, and L_y and L_z are length scales characterizing the plume diffusion. In order to facilitate the practical application of this solution, we express K_y and K_z as

$$K_y = 0.5 U d\sigma_y^2/dx, \quad K_z = 0.5 U d\sigma_z^2/dx \quad (3)$$

where σ_y and σ_z are the widely used Gaussian plume dispersion parameters. This will permit utilization of the empirical data on these parameters for a variety of meteorological and terrain conditions.

Parameterization of Concentration

In order to parameterize and simplify the expressions for concentration, we define, following Rao^{1,2}, the following nondimensional "capped" quantities:

$$\hat{V}_d = V_d/U, \quad \hat{W} = W/U, \quad \hat{V}_1 = (V_d - W/2)/U, \quad \hat{V}_2 = (V_d - W)/U \quad (4a)$$

$$\hat{x} = x/\sqrt{2}\sigma_z, \quad \hat{z} = z/\sqrt{2}\sigma_z, \quad \hat{H} = H/\sqrt{2}\sigma_z, \quad \hat{\tau}_c = \tau_c U/\sqrt{2}\sigma_z \quad (4b)$$

Using Equations 3 and 4, we can now express Equation 2 as

$$C(\hat{x}, \hat{y}, \hat{z}) = Q/U \cdot g_1(\hat{x}, \hat{y})/L_y \cdot g'_2(\hat{x}, \hat{z})/L_z \quad (5a)$$

$$g_1(\hat{x}, \hat{y}) = \exp(-\hat{y}^2), \quad \hat{y} = y/\sqrt{2}\sigma_y, \quad L_y = \sqrt{2\pi}\sigma_y \quad (5b)$$

$$g'_2(\hat{x}, \hat{z}) = \exp(-\beta^2 - \hat{x}/\hat{\tau}_c) [e^{-r} + e^{-s} \cdot (1 - \alpha)], \quad L_z = \sqrt{2\pi}\sigma_z \quad (5c)$$

where

$$\begin{aligned} \alpha &= 4\sqrt{\pi} \hat{V}_1 \hat{x} e^{\xi^2} \operatorname{erfc}(\xi), \quad \beta^2 = 2\hat{W}\hat{x}(\hat{z} - \hat{H}) + (\hat{W}\hat{x})^2 \\ r &= (\hat{z} - \hat{H})^2, \quad s = (\hat{z} + \hat{H})^2, \quad \xi = \hat{z} + \hat{H} + 2\hat{V}_1\hat{x} \end{aligned} \quad (5d)$$

Equation 5 clearly shows that the concentration depends on the dimensionless ratios V_d/U , W/U , and $x/(U\tau_c)$. The effect of deposition can be seen as a multiplication of the contribution of the image source term, e^{-s} , by a factor $(1 - \alpha)$. The concentration at a ground-level receptor can be obtained by setting $\hat{z} = 0$. Other simplifications are possible, *e.g.*, by setting $\hat{H} = 0$ for ground-level sources, and $\hat{W} = 0$ for gases and small particles with negligible settling. When deposition and chemical transformation are negligible ($\hat{V}_d = 0$, $\hat{W} = 0$, $\hat{\tau}_c = \infty$), Equation 5 reduces to the well-known Gaussian plume model with $g'_2 \equiv g_2 = e^{-r} + e^{-s}$. Note that the horizontal crosswind diffusion is not affected by the removal processes.

Under unstable or neutral atmospheric conditions, when the plume travels sufficiently far away from the source, the pollutant is generally well-mixed by atmospheric turbulence, resulting in a uniform vertical concentration profile between the ground and the stable layer aloft at a height L . This concentration, which is independent of the source height as well as the receptor height, can be calculated as the average concentration in a mixed layer of depth L . Thus, the pollutant concentration in the well-mixed region can be expressed as follows²:

$$C(\hat{x}, \hat{y}, \hat{z}) = Q/U \cdot g_1(\hat{x}, \hat{y})/L_y \cdot g'_4(\hat{x})/L \quad (6a)$$

where $g'_4(\hat{x}) = \int_0^\infty [g'_2/L_z]_{H=0} dz$. For gases or small particles ($\hat{V}_d \neq \hat{W}$), this integration yields

$$g'_4(\hat{x}) = \exp(-\beta^2 - \hat{x}/\hat{\tau}_c) [(\hat{V}_1/\hat{V}_2) e^{\xi^2} \operatorname{erfc}(\xi) - (\hat{W}/2\hat{V}_2) e^{\beta^2} \operatorname{erfc}(\beta)] \quad (6b)$$

where $\xi = 2\hat{V}_1\hat{x}$ and $\beta = \hat{W}\hat{x}$. The expression for large particles ($\hat{V}_d = \hat{W}$) is

$$g'_4(\hat{x}) = \exp(-\xi^2 - \hat{x}/\hat{\tau}_c) [(1 + 2\xi^2) e^{\xi^2} \operatorname{erfc}(\xi) - 2\xi/\sqrt{\pi}] \quad (6c)$$

where $\xi = \hat{V}_d\hat{x} = \hat{W}\hat{x}$. When deposition and chemical loss are negligible, Equation 6 reduces to the familiar Gaussian plume model with $g'_4 \equiv g_4 = 1$. The plume is generally considered to be well-mixed for $x \geq 2x_m$, where x_m is the downwind distance x at which $2.15\sigma_z(x) = L$.

In the region $x_m < x < 2x_m$, where the plume is considered to be trapped between the ground and the stable layer aloft, the mixing depth L should be explicitly included in the concentration algorithms. This can be done by writing the equation for $g'_3(\hat{x}, \hat{z})$ following Rao¹, incorporating multiple reflections of the plume from both the ground and the stable layer. Alternately, the ground-level concentrations in this region can be estimated by linearly interpolating between the concentration values at x_m and $2x_m$ on a log-log plot of concentration versus downwind distance.

Once the ground-level concentration is determined, the surface deposition flux of the pollutant can be calculated directly from $D(\hat{x}, \hat{y}) = V_d C(\hat{x}, \hat{y}, 0)$, where D gives the amount of pollutant deposited per unit time per unit surface area.

Area Sources

The urban area-source emission inventory is developed by dividing the city into equal-sized grid cells, each typically a square of 2-5 km side, and representing the total of all low-level emissions of the pollutant in each grid cell by an equivalent area-source emission. The concentration from an area source is generally calculated by integrating the point-source algorithms over the area. We consider two equal grid squares (see Figure 1a), one of them containing the area-source emissions Q , assumed to be located at the center of the square, and the other containing a ground-level receptor R at its center. The wind U blows along the line from Q to R as shown. Then the surface concentration C_A at R due to the area source Q is given by Rao⁵ as

$$C_A = (Q/U) \int_{x_1}^{x_2} [g'_2(x, 0)/L_z] dx \quad (7)$$

where x_1 and x_2 are the distances from the receptor R to the downwind and upwind edges, respectively, of the emission grid square. Since the two grid squares are equal in size, these distances can also be measured from Q to the upwind and downwind edges, respectively, of the receptor grid square, as shown in Figure 1a.

If deposition and chemical transformation are neglected, and if the urban area-source emissions are assumed to occur at ground-level ($H = 0$), then Equation 7 reduces to

$$C_A = \sqrt{2/\pi} (Q/U) \int_{x_1}^{x_2} dx/\sigma_z \quad (8)$$

In the ATDL urban air pollution model, Gifford and Hanna⁶ used this equation with the assumption $\sigma_z = ax^b$, where a and b are constants depending only on the

atmospheric stability, to derive simple algorithms for the concentrations from area sources.

Equation 7 can be easily adapted to account for distributed urban area sources and multiple receptors^{2,5}. Assuming that $\sigma_z = ax^b$ and $H = 0$ in Equation 7, Rao² outlined an elegant new mathematical approach, based on mass budget considerations, to derive a simple expression for ground-level concentration from area-source emissions. This is schematically illustrated in Figure 1b. For each receptor grid square box formed by the ground surface and two imaginary vertical planes at $x = x_1$ and $x = x_2$, the pollutant mass budget can be written as

$$\text{Incoming flux} - \text{outgoing flux} \pm \text{flux gain/loss due to chemical transformation} \equiv \text{surface deposition flux.}$$

Substitution for the various terms above leads to the final expression² for C_A :

$$C_A = Q/[2(1-b)V_d] \{ g'_4(x_1) - g'_4(x_2) - 1/(U\tau_c) \int_{x_1}^{x_2} g'_4(x) dx \} \quad (9)$$

where $g'_4(x)$ is the point-source algorithm (Equation 6) in the well-mixed region. Equation 9 is computationally efficient^{2,7} because it permits one to use the same subroutine for both point and area sources.

All of the equations given above for C_A ignore horizontal diffusion. This is justified on the basis of Gifford's narrow plume hypothesis⁶, which postulates that the concentration at a receptor is influenced only by the distributed area sources located in a fairly narrow, plume-shaped upwind sector. The concentration downwind of the center of the emission grid is then the same as that if the area source were infinitely wide in the crosswind direction.

Conclusions

In this paper, we have briefly described a realistic methodology for including deposition, gravitational settling, and first-order chemical transformation in applied urban air pollution models. The concentration expressions given here can be thought of as analytical extensions of the familiar Gaussian plume dispersion algorithms to include these removal processes. Empirical values of deposition velocities for a wide variety of pollutants and surface and atmospheric conditions can be found in the literature. Some guidance is provided in Rao^{1,2} for specifying the deposition and settling velocities in the concentration algorithms. These algorithms are now optionally available in EPA's air quality models, MPTER-DS, PAL-DS, INPUFF-2, and PAL-2.

Frequently, the product of a chemical reaction may be the pollutant of primary concern, rather than the reactant itself. A well-known example is the atmospheric transport and transformation of SO₂ to sulfate. In general, the secondary (product) pollutant will have deposition and settling velocities which are different from those of the reactant species, and it may also be directly emitted from the sources. The concentration algorithms for such coupled pollutant species, which are also derived by Rao² from the gradient-transfer model, are considerably more complex than those given here. These algorithms are used in the EPA's multi-source urban air quality model PEM-2 (see Rao⁵), which is designed to predict short term (1 to 24 hr) ground-level concentrations and deposition fluxes of two gaseous or particulate pollutants, with or without the chemical coupling, at multiple receptors.

Acknowledgements

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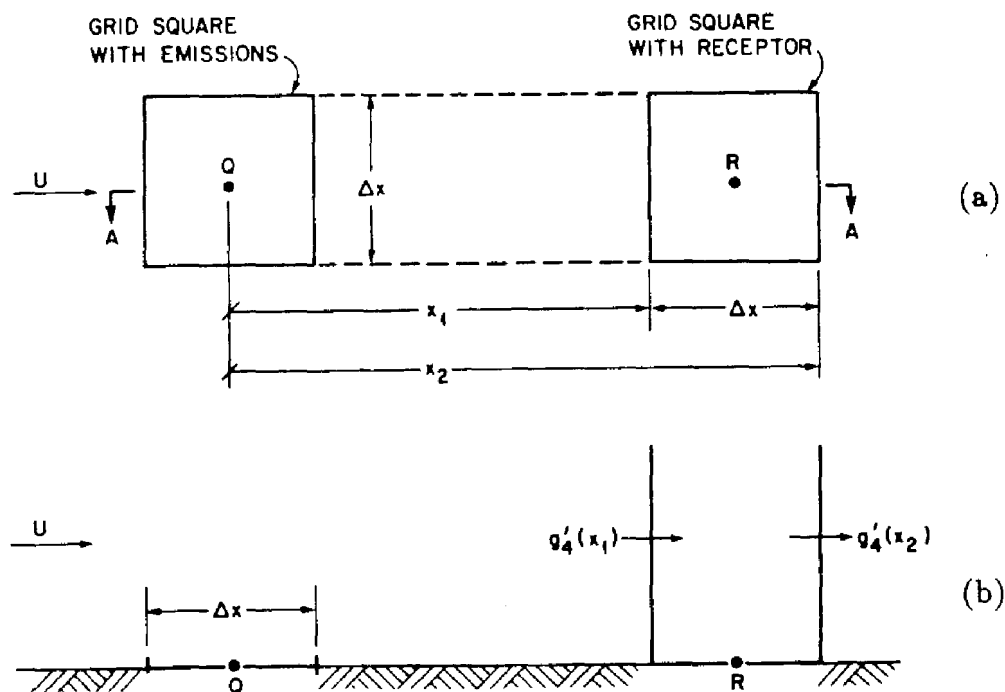


Figure 1. Schematic diagram for area-source algorithms showing (a) an emission grid square and a receptor grid square, and the distances; (b) a cross-section of the receptor grid square, and the incoming and outgoing normalized fluxes of pollutant.

THE INFLUENCE OF MEASUREMENT UNCERTAINTIES ON THE PERFORMANCE OF AIR POLLUTION DISPERSION MODELS

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ABSTRACT

Uncertainties of several classes of air pollution dispersion models are estimated using comparisons with field data for continuous sources in the boundary layer. Source scenarios include ground level point sources, tall power plant stack plumes, dense gas releases, and releases from offshore oil platforms. Model predictions of maximum concentration (independent of position) show typical mean biases of ± 10 to 40% for the best-performing models. Typical root-mean-square errors are about 60% of the mean value, with a range from 30% to 100% for the best models.

The model uncertainties are partly due to measurement uncertainties in input data and in observed concentrations. For example, the wind speed is seldom known within $\pm 10\%$. Monte Carlo methods of estimating the influence of these measurement uncertainties on the model predictions are reviewed.

INTRODUCTION

The past decade has seen a growth in interest concerning the uncertainty in air pollution dispersion models [1,2,3,4]. The old rule of thumb was that dispersion models carried a "factor of two" uncertainty. Recent model development programs have had the objective of significantly reducing this uncertainty, but researchers have discovered that there is a large amount of irreducible uncertainty due to stochastic processes in the atmosphere and due to the limitations of measurements. The purpose of this paper is to provide several examples of the magnitude of the uncertainty associated with air

pollution dispersion models, using results from a variety of sites, source emission scenarios, and models. Methods of quantifying measurement uncertainties and accounting for their effects on model predictions shall be outlined.

EXAMPLES OF UNCERTAINTIES ASSOCIATED WITH AIR QUALITY MODEL PERFORMANCE

We have recently been involved in a broad range of air quality model development and evaluation exercises, involving the use of field data from eight independent full-scale experiments [5,6,7]. The sources in all experiments are continuous point sources within the lowest 100 m of the boundary layer. An overview of the results of each of these studies is given below.

Prairie Grass Experiment: The 1956 Prairie Grass experiment resulted in a comprehensive dataset containing 44 separate runs, where SO_2 was released from a near-surface continuous point source over flat terrain, and detailed supporting meteorological data were taken. This dataset has been analyzed by dozens of researchers and used as the basis for the development and evaluation of numerous dispersion models over the past 30 years. It represents the optimum research-grade field experiment for which data uncertainties are minimized. We used multiple linear regression procedures to fit a simple model to these data, and the resulting model predictions are plotted versus observations in Figure 1 (where concentration, C , is normalized by source emission rate, Q). Maximum concentrations on five downwind monitoring arcs (50 m to 800 m) are included. The model explains about 93% of the variance in the observations, and the rmse or scatter of the predicted C/Q about the best-fit line at any observed C/Q averages about 20 to 30%.

Dense Gas Jet Experiments: Pressurized ammonia and hydrogen fluoride were released continuously from a pipe near the ground, resulting in a dense aerosol jet. Seven separate runs were made (4 for NH_3 and 3 for HF) in which concentrations were observed at downwind distances ranging from 100 m to 3000 m. The performance of 14 hazardous gas models was evaluated with this dataset [5], and the results are summarized in Figure 2. The relative mean bias, $(\bar{C}_o - \bar{C}_p) / 0.5(\bar{C}_o + \bar{C}_p)$, is plotted on the abscissa, and the relative mean square error, $(\bar{C}_o - \bar{C}_p)^2 / \bar{C}_o \bar{C}_p$, is plotted on the ordinate. It is seen that some models perform very poorly, with a relative bias of ± 1.0 (i.e., 100%) and a relative mse of 2 or 3 (i.e., 200 or 300%). However, there is a cluster of 8 models that perform relatively well with relative biases of about 0.0 to 0.4 (i.e., 0 to 40%), and relative mse of about 0.25 to 0.50 (i.e., 25 to 50%). The relative rmse, which equals $(\text{relative mse})^{1/2}$, is therefore about 50 to 70% for these eight models.

Overwater Tracer Experiments: The Offshore and Coastal Dispersion (OCD) model was developed to estimate the on-shore impact of pollutants released from offshore oil platforms. The OCD model was evaluated using 101 individual runs from field experiments at four separate locations [6]. Tracer gas was released at elevations of 10 to 20 m above the water, at distances 1 to 15 km from the shoreline, and concentrations were observed by lines of monitors at the shoreline. Table 1 contains the results of the model evaluation exercise at the four sites, where two or three independent sets of experiments were conducted at each site. The ratio of the means, \bar{C}_p / \bar{C}_o , ranges from 0.65 (i.e., a 35% underprediction) to 2.13 (i.e., a 113% overprediction) over all the experiments, with a median of 1.07. The relative rmse ranges from 0.42 to

Table 1. Comparisons of OCD Model Predicted Concentrations with Observed Concentrations during Overwater Tracer Experiments at Four Locations.

Experiment	Number of Data Points n	Ratio of Means \bar{C}_p / \bar{C}_o	Relative RMSE
			$((C_p - C_o)^2 / \bar{C}_o \bar{C}_p)^{1/2}$
Cameron - Winter	17	0.85	0.60
Cameron - Summer	9	0.80	0.72
Carpinteria - SF ₆	18	2.13	1.17
Carpinteria - Fumigation	9	0.65	0.98
Carpinteria - CF ₃ Br	10	1.07	0.65
Pismo - Winter	15	1.49	0.94
Pismo - Summer	16	1.94	0.90
Ventura - Winter	8	1.23	0.42
Ventura - Fall	9	0.68	0.60

1.17 (i.e., 42 to 117%) from site to site. It is interesting how the model will underpredict at one site and overpredict at another, suggesting that model biases obtained at a single site should not be extrapolated to other sites, and that one should not jump to conclusions if data from only one or two sites are analyzed.

Experiments with Stack Plumes in Urban Areas: For the final example in this section, we present results for the urban Hybrid Plume Dispersion Model (urban-HPDM), which was developed and evaluated using about 80 hours of tracer data from the buoyant plume from an 80 m power plant stack in Indianapolis. Maximum predicted and observed concentrations on downwind arcs ranging from 0.25 to 12 km were considered for a wide range of stability conditions [7]. It was found that the ratio of the means, \bar{C}_p / \bar{C}_o , equaled 1.08 (i.e., a 7% overprediction), and the relative rmse was calculated to be 0.35 (i.e., 35%). There is little variation of the ratio C_p / C_o with wind speed stability, mixing height, and hour, implying that the model generally satisfies the requirement that model errors should be randomly scattered and should not be functions of any input variables. We emphasize that the same data were used to both develop and evaluate the model. In the next few months, the model will be evaluated with about 80 hours of "independent" data from the same experiment, which have been reserved especially for the final evaluation exercise.

UNCERTAINTIES IN METEOROLOGICAL MEASUREMENTS

Part of the uncertainty in air pollution dispersion model predictions is due to uncertainties in input parameters, such as wind speed and stability [8]. We have surveyed a large number of reports and journal articles in order to estimate the meteorological data uncertainties listed in Table 2. It is assumed that typical averaging times of 10 to 60 minutes are used. Furthermore, it is recognized that there are two classes of instruments in operation: research-grade and routine, where recommended QA/QC procedures are followed in all cases. In general, remote sounders are found to provide adequate estimates of mean wind speed and direction, but do not yield satisfactory observations of the turbulence components, σ_v and σ_w [9]. Routine wind sensors are subject to large errors when the wind speed drops below the threshold (0.5 to 1.0 m/s), and mixing depth observations become inadequate at values less than about 200 m.

Table 2. Typical Uncertainty in Meteorological Measurements (10-60 min avg.)

Parameter	Instrument	Uncertainty
Wind Speed	Sonic	0.1 m/s (threshold < 0.1 m/s)
	Cups, Props,	0.3 m/s (threshold 0.5 - 1.0 m/s)
	Remote Sounders	1.0 m/s
Wind Direction	Research-Grade	2°
	Routine	5°
	Remote Sounders	10°
Lateral Turbulence (σ_y)	Research Grade	0.1 m/s
	Remote Sounder	0.5 m/s
Vertical Turbulence (σ_w)	Research Grade	0.1 m/s
	Remote Sounder	0.5 m/s
ΔT	Research Grade	0.1 K
	Routine	0.4 K
	Radlosonde	100 m
Mixing Depth	Remote Sounder	100 m (minimum 50 m)

ESTIMATING THE EFFECTS OF MEASUREMENT UNCERTAINTIES

There are two methods for estimating the effects of uncertainties in meteorological observations on dispersion model predictions: (1) an analytical method based on differentiation of the model equations and (2) a Monte Carlo method where the model is run many times for randomized input data [10]. The first method is practical only if the data uncertainties are small (< 10%) and if the model equations are relatively simple and can be easily differentiated. Because it is possible to run most models on a computer in minimal time, the Monte Carlo method (2) is the choice in most uncertainty analyses. In order to apply this method, it is necessary to estimate the means and variances for each input meteorological parameter. To be strictly correct, known correlations among meteorological variables (e.g., very strong stable conditions cannot occur with high winds) should be accounted for when the random variables are selected. However, in most applications of the Monte Carlo method, these correlations are ignored.

A simpler alternative is to run the models for only two extreme values of each input parameter, rather than hundreds, in order to bracket the solution, or determine the sensitivity of the solution to variations in the parameter. To demonstrate this procedure we have applied the SLAB dense gas model to an area source emission of chlorine gas, where $Q = 5$ kg/s, source radius = 5 m, source duration = 5 min, and concentration averaging time = 5 min. The base calculation is made for a wind speed u of 5 m/s, a surface roughness z_0 of 0.10 m, and a Monin-Obukhov length L of ∞ m (i.e., neutral stabilities). The model was then run for $u = 4$ m/s and 6 m/s, $z_0 = 0.05$ and 0.15 m, and $L = -100$ m and 100 m, where only one input parameter at a time is varied. These variations in L represent uncertainties in stability of about one Pasquill-Gifford class. Resulting centerline concentration predictions at downwind distances of 100, 800, and 2800 m are listed in Table 3. It is seen a $\pm 20\%$ variation in wind speed causes a $\pm 20\%$ variation in predicted concentration. The variation in predicted concentrations is about ± 30 to 50% for the stated variation in stability class, and is about ± 15 to 25% for the stated variation in roughness length. If these input parameters are not known with any better accuracy, then it can be concluded that errors in model predictions of at least 50% are possible.

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Table 3. Sensitivity Runs of SLAB Model for Chlorine Pool.

u (m/s)	z ₀ (m)	L (m)	Comment	Concentration (ppm) at Downwind Distances		
				100 m	800 m	2800 m
4	0.10	∞	Low Wind	2010	46.6	3.84
5	0.10	100	Stable	2180	53.6	4.66
5	0.05	∞	Less Rough	2130	46.3	3.84
5	0.10	∞	Base Case	1660	37.1	3.14
5	0.15	∞	More Rough	1420	31.9	2.75
5	0.10	-100	Unstable	1190	24.0	2.00
6	0.10	∞	High Wind	1390	30.7	2.69

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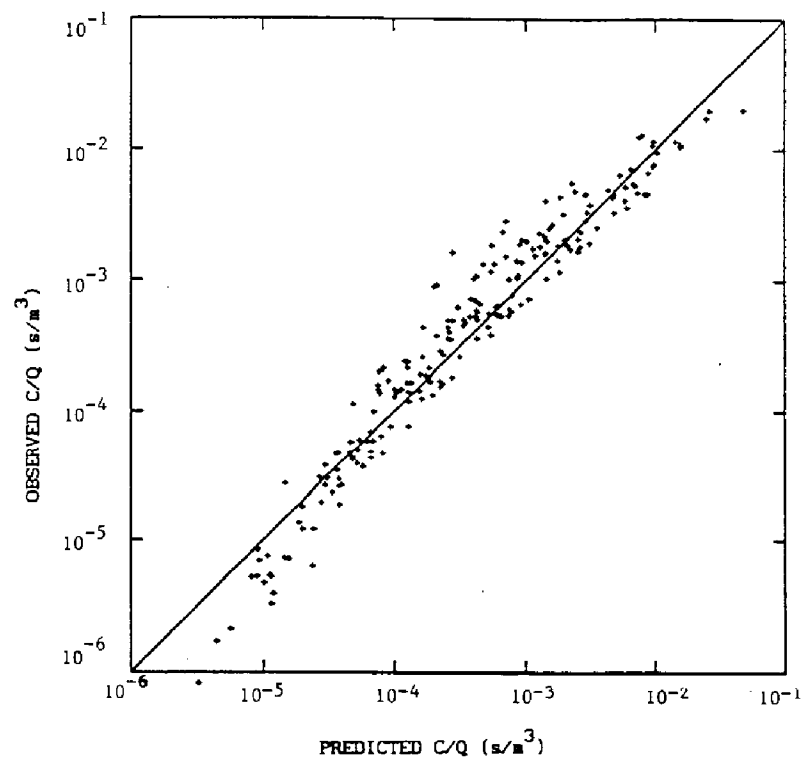


Figure 1. Comparison of observed C/Q at the Prairie Grass site with values predicted by multiple linear regression procedure. 93% of the variance in the observed C/Q is accounted for by the predictions.

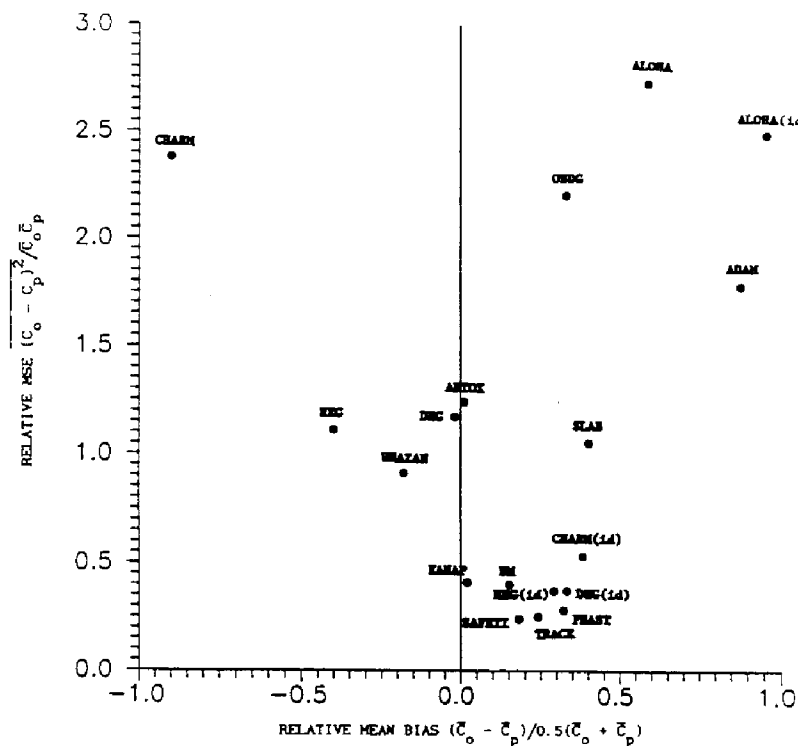


Figure 2. Relative mean bias and mean square error, for concentration predictions for 14 hazardous gas model compared with observations of two dense gas jets.

FLOW AND DISPERSION OF POLLUTANTS WITHIN TWO-DIMENSIONAL VALLEYS

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Wind-tunnel experiments and a theoretical model concerning the flow structure and pollutant diffusion over two-dimensional valleys of varying aspect ratio are described and compared. Three model valleys were used, having small, medium, and steep slopes. Measurements of mean and turbulent velocity fields were made upstream, within and downwind of each of these valleys. Concentration distributions were measured downwind of tracer sources placed at an array of locations within each of the valleys. The data are displayed as maps of terrain amplification factors, defined as the ratios of maximum ground-level concentrations in the presence of the valleys to the maxima observed from sources of the same height located in flat terrain. Maps are also provided showing the distance to locations of the maximum ground-level concentrations. The concentration patterns are interpreted in terms of the detailed flow structure measured in the valleys. These data were also compared with results of a mathematical model for treating flow and dispersion over two-dimensional complex terrain. This model used the wind-tunnel measurements to generate mean flow fields and eddy diffusivities, and these were applied in the numerical solution of the diffusion equation. Measured concentration fields were predicted reasonably well by this model for the valley of small slope and somewhat less well for the valley of medium slope. Because flow separation was observed within the steepest valley, the model was not applied in this case.

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Introduction

This report presents results of the Joint Soviet-American Work Program for studying air flows and dispersion of pollutants within valleys¹. It is a natural complement to earlier work² wherein similar measurements were made over two-dimensional hills. An extensive data set was collected in a wind tunnel on the flow structure and concentration fields resulting from sources placed within valleys with different width-to-depth ratios. In addition to furthering basic understanding, one of the main purposes of the experiments was to test the performance of a diffusion model for calculating ground-level concentrations (glcs) resulting from point sources placed within the valleys.

The primary results are presented in terms of terrain amplification factors (TAFs), defined as the ratios of maximum ground-level concentrations in the presence of the valleys to the maxima from sources of the same height in flat terrain. This definition does not involve the locations of the maximum glcs, which will generally occur at very different downwind distances in the two situations. We present the primary results as contour plots of constant TAF. This allows the further introduction of "windows" of excess concentration. If a source is far enough upstream of the valley and the pollutant is released at low level, the maximum glc will occur upstream of the valley, so that the effect of the valley will be negligible. If the source is tall enough, the maximum glc will occur downstream of the valley, so that, again, the effect of the valley will be negligible. If pollutants are released within the valley, the TAF will generally exceed unity, and its value will depend upon the source location within the valley. Hence, a "window" will exist such that pollutants emitted within that window will result in "excessive" glcs.

Lawson *et al.*³ have presented "windows" of excess concentration (for typical shapes of two- and three-dimensional hills) that extended as far as 10 to 15 hill heights upstream and downstream of the hills. The purpose of the current study was to determine to what extent valleys might influence maximum glcs, that is, to establish windows of excess concentration for typical valley shapes. The shapes chosen were two-dimensional, with three different aspect ratios, $n=a/h=3, 5$, and 8 , where a is the valley half-width, and h is the valley depth. These shapes were chosen to represent a fairly typical range of realistic valley shapes. The maximum slopes were 10° (valley 8), 16° (valley 5), and 26° (valley 3). The flow structure in these valleys differed dramatically from one another. In valley 8, the flow did not separate and, to some extent, resembled potential flow. In valley 3, the flow clearly separated on the upstream slope, and a mean recirculation region was formed inside the valley. In valley 5, the separation might be described as *incipient*; the *mean* flow was downstream everywhere, but instantaneous flow reversals were commonly observed. Thus, pollutants emitted within this flow were frequently wafted back and forth before being transported downstream.

Concurrently with the measurement program, a theoretical model⁴ was used to calculate terrain amplification factors for sources located within the valleys. This model used wind-tunnel data on the flow structure as input for numerical solution of the turbulent diffusion equation. The model provided quite reasonable predictions of TAFs for the valley of intermediate slope and somewhat better predictions for the gently-sloped valley. Because the model cannot handle separated flows, it was not applied to the steep-sloped valley.

Apparatus, Instrumentation, and Measurement Techniques

The model valleys were placed within the EPA Meteorological Wind Tunnel, which has a test section 3.7 m wide, 2.1 m high and 18.3 m long. The approach flow was a simulated atmospheric boundary layer. Extensive measurements of both the flat-terrain boundary layer and the flow structure within the valleys were made using hot-wire and pulsed-wire anemometry. Ethane gas, used as a tracer, was released from numerous

positions within each valley through a perforated sphere to simulate a neutrally buoyant point source. Concentration measurements were made downstream using flame-ionization detectors. More extensive descriptions of the experimental apparatus and measurement techniques may be found in Snyder *et al.*⁵ or Khurshudyan *et al.*¹.

Presentation and Discussion of Experimental Results

The pulsed-wire anemometer proved to be quite useful within the very highly turbulent, separated flows within the valleys, because it can sense flow reversals. Probability density distributions of longitudinal velocity fluctuations were constructed from the pulsed-wire measurements. They showed that at the lowest levels within valley 5, mean velocities were quite small, but instantaneous flow reversals were very common (up to 40% of the time). In valley 3, mean velocities were negative below $h/4$, very close to zero at $h/2$, and some reversals occurred even at the valley top h . In spite of the flow reversals and very large turbulence intensities (up to 170%), for many practical purposes, the distributions were closely Gaussian in character.

Mean streamlines were calculated from the mean velocity measurements within the valleys (Figure 1). At first glance, the streamline pattern over valley 8 is reminiscent of potential flow; but closer examination reveals it is asymmetrical, with the lower streamlines being slightly closer to the surface on the downwind slope than on the upwind one. The streamline pattern over valley 5 is clearly asymmetrical, and because the streamlines diverge strongly away from the surface, it is clear that the velocity is reduced markedly at the valley center; indeed, it appears that a stagnation region exists in the valley bottom. In valley 3, the streamline pattern clearly shows a recirculation region, with separation occurring a short distance down the upwind slope and reattachment occurring about halfway up the downwind slope. The three valley shapes thus result in three fundamentally different flow patterns. These basic flow structures are fairly typical and cover the range of patterns to be observed at full scale, albeit in neutral stratification.

Figure 2 illustrates some typical comparisons between surface concentration profiles measured from sources placed above the valley centers and that from a source of the same height in flat terrain. In all cases, the stack height H_s was equal to one-half the valley depth h . x_s denotes the distance from the source. The increased concentrations caused by the valleys are dramatic and the TAFs range from about 2.5 in valley 8 to about 12 in valley 3. As the concentration increases, the distance to the maximum decreases. The location of the maximum for valley 3 was actually slightly upwind of the source. For valley 5, the location of the maximum glc was downstream, but very close -- about 2 stack heights away -- and the TAF is about 6.

Measurements such as these were made at an array of source locations and heights in the vicinity of each of the valleys, and the TAFs were determined for each location. Maps of these TAFs are shown in Figure 3, where isopleths of constant TAF have been drawn. The first impression is that the patterns are symmetrical about the vertical centerline, but closer examination reveals some asymmetry. Nevertheless, the near-symmetry and the overall similarity in shape amongst the three valleys is quite surprising in view of the very different flow patterns observed. In contrast, the magnitudes of the maximum TAFs differ widely, from 2.5 in valley 8 to 17 in valley 3. These differences, of course, reflect the effects of the different flow structures.

Contours with TAF values of 1.4, 2, 4, etc., have been drawn where appropriate. Note that these contours form "windows" within which the maximum glc exceeds the glc that occurs in flat terrain by 40%, 100%, 300%, etc. The longitudinal extent of the window of 40% excess concentration extends over approximately 60% of the width of valley 8, 80% of the width of valley 5, and more than 90% of the width of valley 3. The vertical extent of the 40% window is 1.5, 2.0, and 2.5 valley heights above the valley top for valleys 8, 5, and 3, respectively.

Application of the data in Figure 3 is straightforward. Let us consider a source which is located in the center of a rather broad valley, say one similar in shape to valley 8; and the height of the source is half the valley height. Figure 3c suggests that the maximum glc would be about 2.5 times that expected from a source of the same height but located in flat terrain. On the other hand, if the valley were considerably narrower, say close to valley 5, Figure 3b suggests the maximum glc would be about 7 times as large. Although precise interpolation of these results for valleys intermediate in shape to those examined here may be difficult, the results allow us to place some useful limits on the effects of valleys of intermediate shape.

Figure 4 shows the loci of source positions leading to the same locations of maximum glc. These loci have been identified by marking them with the position of the maximum glc (in valley heights from the centers of the valleys). Note that the "undisturbed" or flat-terrain loci (dotted lines) are simply parallel, nearly straight, diagonal lines. Within the valley, these loci are distorted, as shown by the solid lines. The diagrams may be used as follows: for any given source position, we may plot that position on the diagram, then follow the locus to the ground; the intersection of that locus with the ground is, of course, the location of the maximum glc. Conversely, from a knowledge of the location of the maximum glc, we may use these diagrams to determine the line along which the source was positioned. These loci become highly distorted near the valley centers, and the steeper the valley, the higher the distortion. As the distance (both longitudinal and vertical) from the valley center increases, these loci gradually relax to their undisturbed or flat-terrain values.

Numerical Model and Comparisons with Experimental Results

One of the main purposes of the experimental study described above was to test the applicability of a diffusion model for the evaluation of maximum glcs resulting from elevated continuous point sources placed in a curvilinear neutral atmospheric boundary layer. The model used data from the wind-tunnel measurements of wind velocities and turbulence characteristics as input parameters to calculate two-dimensional, mass-consistent flow fields. These flow fields were then applied in the numerical solution of the diffusion equation. Such a model was developed³ primarily for evaluation of pollutant dispersion in complex terrain. The present version of the model does not incorporate a longitudinal diffusion term, and therefore does not calculate the spread of pollutants in separated flows. Thus, no attempt was made to apply the model to valley 3, and calculations were made only for valleys 5 and 8.

Contour maps of constant TAF as predicted by the model are shown in Figure 5. These are to be compared with the measurements shown in Figure 3. The maps for valley 8 show generally similar overall patterns, but they differ in several details. The vertical extent of the 40%-excess window (the TAF = 1.4 contour) extends to about 1.5 h based on the measurements, but to only 1.25 h based on the model predictions. The horizontal extent of the measured window is larger than that of the model-predicted window. The model-predicted window is shifted slightly upstream and, whereas the resolution of the grid used for the experimental measurements was rather coarse, a hint of an upstream shift is also observed there. The model generally predicts larger TAFs to occur at lower elevations, whereas the measurements show elevated maxima. Both predicted and observed TAFs were less than unity when the source was at the upstream or downstream edge of the valley. Maximum TAF values are quite close to one another. Similar statements may be made when comparing the calculated and observed TAF maps for valley 5, but the differences are somewhat larger.

Conclusions

The model valleys cover the range of a majority of valleys to be found at full scale, at least in terms of the basic classes of flow structure that may be observed. Valley 8 was rather gentle in slope, and the flow over it may be characterized as relatively smooth and well-behaved. Valley 5, being steeper in slope, caused the flow to separate intermittently, but not in the mean. In valley 3, the steepest, the flow

clearly separated a short distance from the upstream edge, and a recirculating flow was formed within the valley. Pollutants released at the same relative locations within each of these valleys behave very differently from one another, and the resulting surface concentration patterns are dramatically different.

The overall effects of the valleys on surface concentrations are characterized in terms of terrain amplification factors (TAFs). Maps of these TAFs are provided for each valley. Also provided are maps detailing the distances to locations where the maximum ground-level concentrations occur. These maps allow a practitioner to quickly and easily assess the likely impact of a source located in a valley and to identify the location where that maximum impact will occur.

A two-dimensional theoretical model that uses a variational analysis technique was applied to the wind-tunnel measurements to produce mass-consistent mean wind fields. Measurements of the turbulent fluctuating velocities were also used to calculate vertical and crosswind eddy diffusivities. The diffusion equation was then solved numerically to obtain maximum ground-level concentrations from elevated point sources of various heights near valleys 8 and 5, as well as over flat terrain. Comparison of calculated and measured TAFs for valley 8 showed satisfactory agreement. Valley 5 exhibited more severe streamline distortion and a stagnation region with large fluctuating velocities near the bottom of the valley, and therefore the differences between calculated and measured TAFs were significant in some cases.

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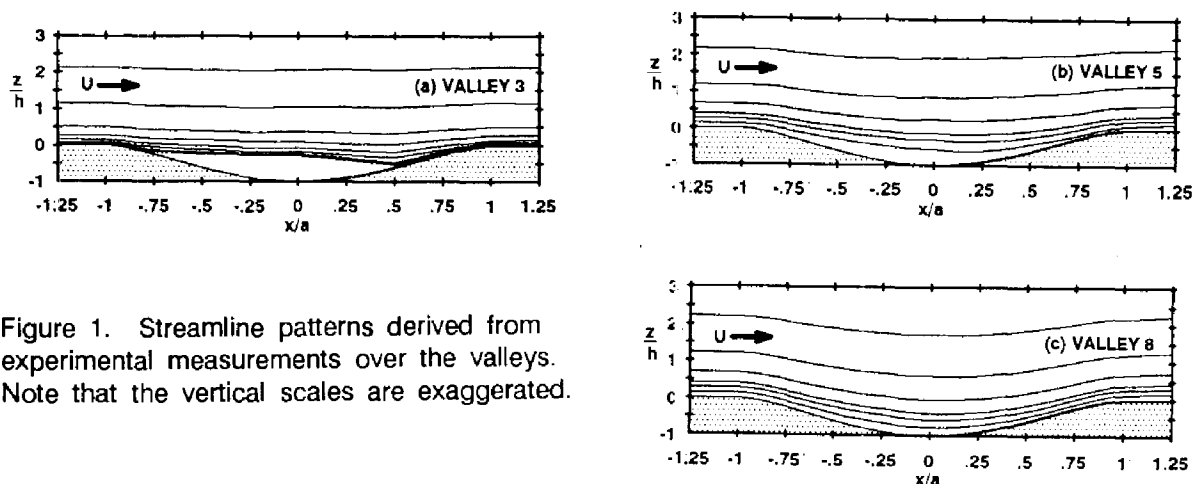


Figure 1. Streamline patterns derived from experimental measurements over the valleys. Note that the vertical scales are exaggerated.

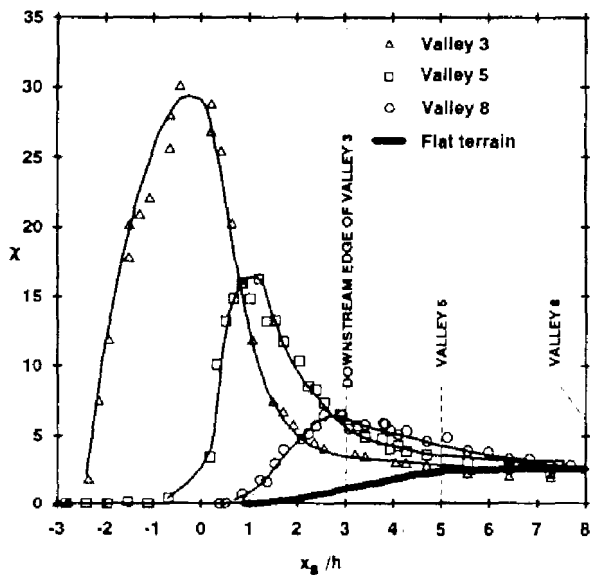


Figure 2. Comparison of surface concentration profiles from sources placed above valley centers with one from source of same height in flat terrain. $H_s = h/2$.

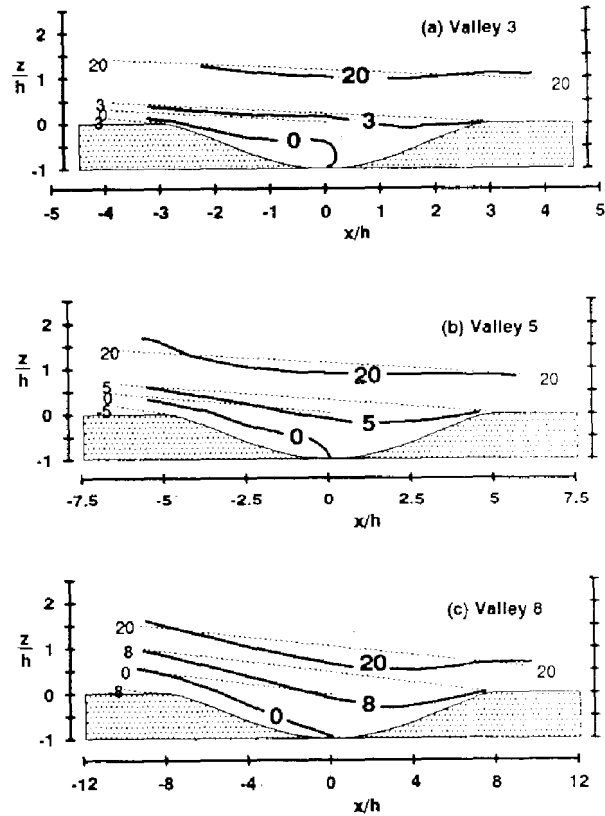


Figure 4. Distance in valley heights from valley center to location of maximum ground-level concentration. Flat terrain values are indicated as dotted lines.

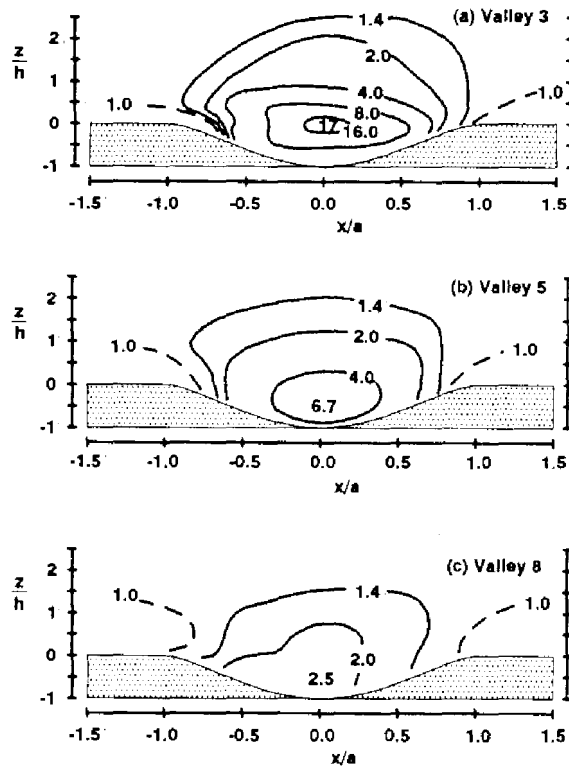


Figure 3. Contours of constant terrain amplification factor derived from experimental measurements.

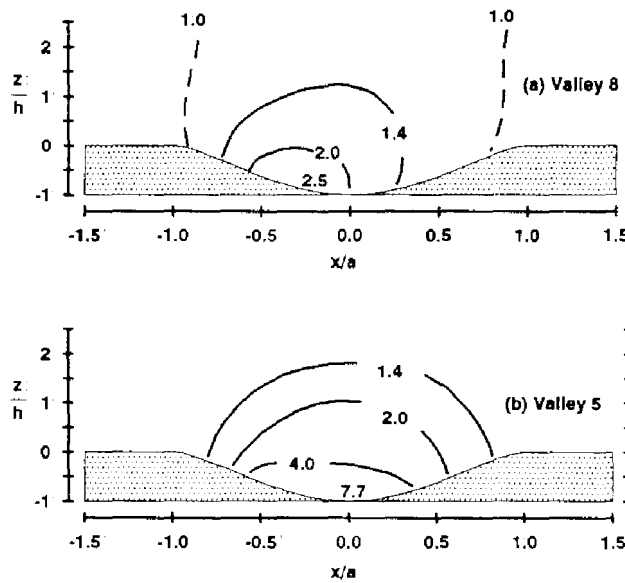


Figure 5. Contours of constant terrain amplification factor derived from model calculations.

WIND-TUNNEL MODELING OF THE DISPERSION OF ODORANTS AND TOXIC FUMES ABOUT HOSPITALS AND HEALTH CENTERS

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Abstract. This paper presents results from wind-tunnel dispersion studies performed around a hospital health center. Large research and teaching hospitals or health centers frequently include animal laboratories, contagious disease wards, incinerators, diagnostic laboratories, and radiological treatment facilities. The resulting building complex thus includes chemical fume hoods, exhaust ducts and short stacks distributed almost randomly over the building roofs and walls. Such activities are sources for odorants, air-borne bacteria or viruses, exotic and often toxic chemicals, and radioactive gases. Wind-tunnel simulations of the resulting transport of toxic or odorous scalar products are often needed to optimize the placement of air handling units or mitigate existing re-entrainment conditions.

Introduction

The concentration field produced by a source located on or near a hospital complex can be significantly modified from that predicted by conventional diffusion formulae. Such formulae contain the implicit assumptions that the flow field has straight parallel streamlines, modest velocity gradients, and distribution of turbulence energy and length scales which result from surface features that remain unchanged over long distances. Near large hospital buildings the flow field becomes highly complex. Curved streamlines, sharp velocity discontinuities, and non-homogeneous turbulence disperse effluents in a complicated manner uniquely related to source configuration and building geometry. Research and teaching hospitals or health centers in particular often contain laboratories, disease wards, incinerators, and radiological treatment facilities which can release particularly noxious odorants and toxic gases. These facilities tend to grow

and add extensions, wings or entire buildings which complicate the placement of air handling units intended to mitigate re-entrainment of effluents.

Some general guidance exists about the flow field around building complexes in the ASHRAE Handbook and Product Directory, and monograph chapters on turbulent diffusion near buildings.^{1,2,3} If concentrations predicted by such methods are marginal or the building configuration is unique then field or laboratory (wind tunnel) sampling at critical locations are proposed. This paper presents the results of case studies of ventilation problems associated with such a health center.

Cases studies to be considered include a) dispersion from fume hoods and exhausts of the University of Colorado Health Sciences Center (UCHSC), Denver, and b) transport of traffic exhaust into air handlers for the proposed Biological Research Center (BRC), University of Colorado, Denver.^{4,5}

Fluid Modeling Criteria

Successful fluid modeling requires simulation of the characteristic turbulent scales of the atmospheric boundary layer and the replication of scaled flow around hospital buildings. Similarity criteria and wind-tunnel metrology are reviewed by Snyder (1981), Plate (1982), and Meroney (1986).^{6,7,8} Critical to accurate estimation of isolated plume dispersion will be the reproduction of approach wind and turbulence profiles as characterized by friction velocity, u_* , and roughness length, z_o , or velocity profile power-law exponent, α .

Often atmospheric turbulence may cause only weak effects compared to the turbulence generated by a hospital complex and local terrain. Yet the magnitude of the building induced perturbations depends upon the incident flow turbulence scale and intensity, details of the hospital shape and surface roughness, and size of the hospital compared to the boundary layer depth. Geometrical scaling implies that the ratio of the hospital building height to length scale must be matched and, of course, that all other building length scales be reduced to this same ratio.

Golden (1961) measured the concentration patterns above the roof of model cubes in a wind tunnel.⁹ Frequently, modelers quote Golden's experiments as justification for presuming dispersion invariance when obstacle Reynolds numbers exceed 11,000. Halitsky (1968) observed that for dispersion in the wake region, no change in isoconcentration isopleths from passive gas releases was found to occur for values of Reynolds number as low as 3300.¹⁰

In addition to modeling the turbulent structure of the atmosphere in the vicinity of a test site it is necessary to properly scale the plume source conditions. When one considers the dynamics of gaseous plume behavior the following nondimensional parameters of importance are identified: Momentum flux ratio, $\rho_s W_s / \rho_{ref} U_{ref}$; Densimetric Froude number, $Fr = \rho_{ref} U_{ref}^2 / [(\rho_s - \rho_{ref})L]$; and plume Reynolds number, $Re_p = W_s D / \nu$. Exhaust gases released from fume hoods and small ventilators are typically at ambient temperatures and densities; thus, model plumes are also set to ambient density. Plume exit Reynolds number need only be large enough to ensure turbulent conditions, i.e., $Re_p > 2500$.

Data Acquisition and Analysis Techniques

The experiments were performed in the Environmental Wind Tunnel (EWT) of the Fluid Dynamics and Diffusion Laboratory at Colorado State University. This wind tunnel, especially designed to study atmospheric flow phenomena,

incorporates special features such as an adjustable ceiling, a rotating turntable and a long test section to permit adequate reproduction of micrometeorological behavior. Mean wind speeds of 0.1 to 15 m/sec in the EWT can be obtained. Boundary-layer thickness up to 1.2 m can be developed over the downstream 6 m of the EWT test section by using vortex generators at the test section entrance and surface roughness on the floor. The EWT roof is adjustable in height to reduce blockage and permit the longitudinal pressure gradient to be set at zero.

Flow Visualization Techniques. A visible plume was produced by passing the metered simulant gas through a smoke generator (Fog/Smoke Machine manufactured by Roscolab, Ltd.) and then out of the modeled stack. The visible plumes for each test were recorded on either VHS or S-VHS video cassettes with a Panasonic Professional/Industrial camera/recorder system (AG-450). Flow visualization provides insight into how architectural features lead to shortened dispersion paths between source and receptor locations. Often visualization suggests changes in exhaust location, stack height, or other architectural modifications which mitigate re-inhalation situations. Observations of visualization tests were examined to note the presence or absence of phenomena such as building downwash, plume descent, and cavity vortices.

Concentration Measurements. The experimental measurements of concentration were performed using a Hewlett Packard gas-chromatograph and sampling systems designed by Fluid Dynamics and Diffusion Laboratory staff. The lower limit of measurement is imposed by the instrument sensitivity and the background concentration of tracer within the air in the wind tunnel. Background concentrations were measured and subtracted from all data quoted herein. Concentrations were presented as normalized concentrations, $K = \chi U_w / Q$, for all tests.

Test Program and Data

Exhaust fumes from seed storage and drying operations, animal pens, and chemical fume hoods are released at many points over the roofs of the UCHSC. Occasionally these fumes enter the air-handling units resulting in odors and contaminated air throughout the School of Medicine. Another problem is to locate inlet ventilators for the new Biomedical Research Center (BRC) in order to avoid vehicle exhaust entrainment.

A physical modeling study of the UCHSC vent buildings was performed to assist in predicting environmental impacts for several proposed stack-building configurations. This involved:

- 1) The 1:150 reduced scale construction of all buildings within 900 feet of the School of Medicine site,
- 2) The placement of this model into a wind tunnel facility with the appropriate upwind roughness for this site,
- 3) Acquisition of velocity and turbulence profiles approaching and at the modeled UCHSC site,
- 4) Video taping of six different model plumes for 16 different wind directions, and
- 5) Concentration measurements at either 48 (for the School of Medicine) or 34 (for the Biomedical Research Center) different sampling locations for two wind speeds and eight wind directions,

Model Construction. Based on atmospheric data over the UCHSC area, the size of the concentration grid, and modeling constraints discussed above, a model scale of 1:150 was selected. Since the Environmental Wind Tunnel has a 3 m turntable this allowed the reduced scale construction of all

significant buildings within a 900 foot radius of the UCHSC site. The terrain upwind of the turntable area was modeled with a generic 2.54 cm roughness.

Ventilator buildings incorporated large ventilator plenums and accurate placement of inlet and exhaust openings. The primary ventilator buildings are the Biomedical Research Center (BRC) and the School of Medicine (SOM). Sampling and source points surveyed during concentration measurements are indicated for the UCHSC in Figure 1 and for the BRC in Figure 2.

Test Plan School of Medicine. The emissions from the Research Bridge and Hospital roofs, a highly toxic gas from a stack on the hospital (ETO), and fumes from a stack on the SOM roof (EF-91) were all simulated. Additionally the intakes on the Hospital roof, on the roof of the SOM, and on the SE annex of the SOM were modeled.

Test Plan Biomedical Research Center. The emission from the Research Bridge roof tops, the emission from the BRC roof top, and the traffic from the Colorado Boulevard were evaluated. The observations were divided into building downwash, plume descent and vortices situations.

Discussion of Typical Results

Selection of the final intake and exhaust stack configuration for the UCHSC and BRC sites will be based upon the consideration of its visual appearance, zoning regulations, and mitigation of environmental impact. The environmental effects of exhaust from the ventilator stacks will depend upon traffic volume, ventilator flow rates, state and federal ambient air-quality regulations, building and plume aerodynamics, and local meteorology. This study evaluates through fluid modeling the influence of building and plume aerodynamics on plume dilution.

Conclusion from smoke visualization tests. Major conclusions drawn from observations of the visualization tests are as follows:

1. Emissions from the stack on the SOM roof top do not appear to have much impact on the SOM itself. However, with a easterly wind there is some downwash into the larger of the two roof airhandler courtyards on the SOM. Some building downwash is also evident with a NE wind into the courtyard on the southern side of the SOM.
2. Emissions from the Research Bridge roof top tend to completely engulf any region downwind. Consequently there could be a considerable collection of pollutants from this source which may accumulate in regions where the air stagnates. The Plaza to the SE of the BRC being one such example.
3. There is some downwash of the exhaust vented from the BRC into the adjoining courtyard, especially for N,NW and SW wind directions. However, for the most part the fumes do not appear to have a strong effect upon the proposed BRC itself.
4. Vehicle emissions from Colorado Boulevard did have a considerable effect on the BRC. With wind coming from the N, the eddy in the wake of the BRC tends to draw the pollutants back into the BRC's SE courtyard. For winds coming from the NE, E, and SE directions, the auto emissions tend to impinge on the BRC, concentrating along its west and north sides. This results in high concentration on the intakes proposed for the west side of the building. But with winds coming from the SW and W directions, the vortices caused by the obstacle of the BRC

building tends to sweep the traffic exhaust westward or away from the building, that would cause low concentration at the proposed intake locations.

Conclusions from concentration measurements. By maintaining flow similarity between model and field conditions, relative concentrations (χ/Q) for a given source configuration, building configuration and wind direction will be invariant. The wind tunnel relative concentration measurements for the UCHSC building complex will be the same as those that could be obtained during full-scale measurements under the same ambient conditions.

Variation of wind orientation produces a wide variance in sample concentrations. For the SOM Figure 3 shows concentrations measured at all the sampling locations from the three exhaust sources for the NE wind direction. Because the ETO stack is close to the intakes on the Hospital roof top and the exit velocity for the stack is large, the Maximum K concentration reaches a value as high as 6,000. Concentrations at the intakes on the Hospital roof top are always higher than the other locations sampled.

For the BRC Figure 4 indicates concentrations measured at the sampling points for a east wind direction for each exhaust source. Sampling point #19 detects the highest K concentration value measured during the entire test (13,000 from the traffic exhaust). This indicates that the traffic exhaust strongly effects the proposed intake locations. The wind coming from the E produces 20 times higher K coefficient than the wind coming from the west. This phenomenon was also shown during the visualization program.

Based on the concentration data acquired during this study, there were two recommendations as follows:

1. The intakes on the Hospital roof top should be closed and removed in order to avoid the highly hazardous ETO stack.
2. The best location for the potential intakes at the Biomedical Research Center should be on the roof top near the sampling point # 4 of that building to avoid the traffic exhaust.

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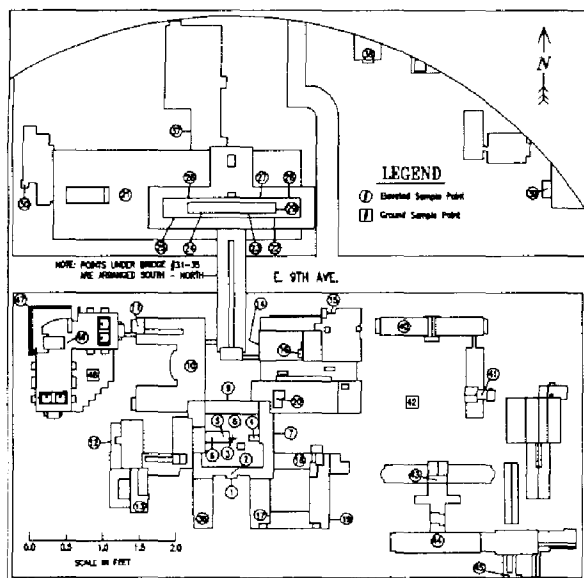


Figure 1 Sampling Point Diagram for the School of Medicine

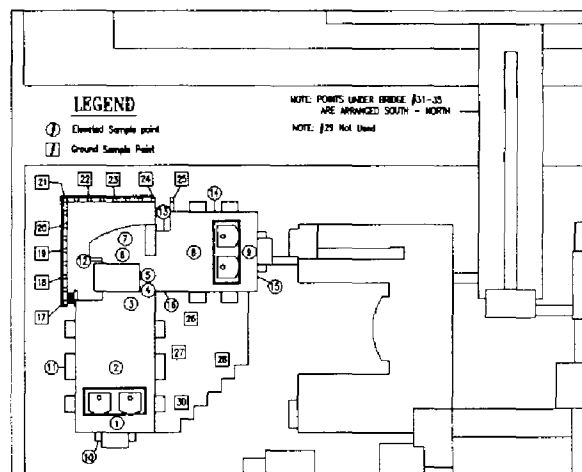


Figure 2 Sampling Point Diagram for the Biomedical Research Center

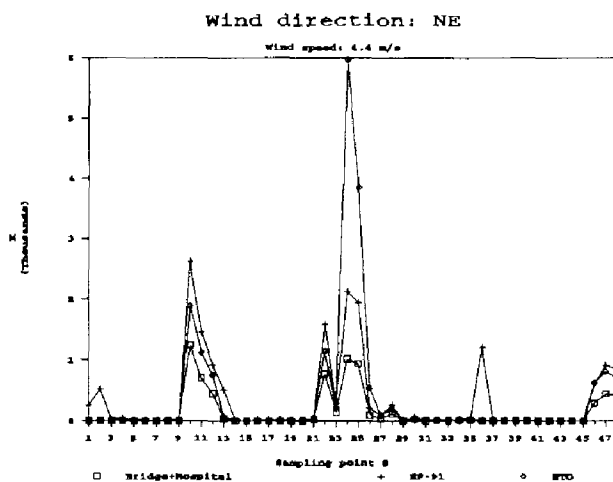


Figure 3 Concentration Level at NE Wind Direction for Low Speed Conditions

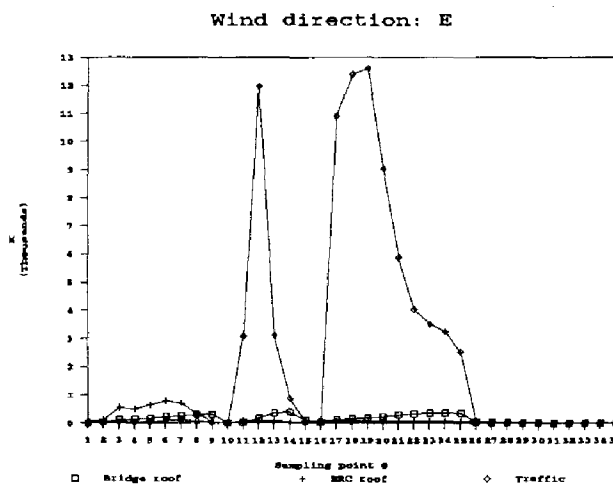


Figure 4 Concentration Level for East Wind Direction and Low Speed Conditions

ESTIMATING EXPOSURES DOWNWIND OF ISOLATED BUILDINGS

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Introduction

Using results from video-image smoke dispersion experiments^{1,2} recently conducted in the Environmental Protection Agency (EPA) wind tunnel, an evaluation was conducted of the application of a finite line source model for simulating the dispersion of a continuous nonreactive, nondepositing point source release, centered at ground-level on the leeward side of a building. The model estimates the average concentrations at surface receptors within the cavity and wake region of the building. With the vertical dispersion effects simulated using an empirical estimate of the nondimensional crosswind integrated concentration as a function of scaled distance downwind from the building, the model construct allows incorporation of results from various experiments. The dispersion induced by the building is seen to result from a superposition of two dispersive processes, that induced by the building, and that which would have occurred if the building were not present. For buildings not oriented perpendicular to the predominate wind flow, an additional dependence of building orientation would occur. Although some work has been accomplished on wind orientation effects^{3,4}, it was decided to limit this discussion to the simplest case of flow perpendicular to the building, and await the processing of data regarding wind orientation effects just recently collected in the EPA wind tunnel during the summer of 1989.

Modeling Equations

The concentration χ downwind from an ideal continuous point source release of Q mass per unit time is often approximated as having a Gaussian lateral dispersion as,

$$\chi = \frac{X_y}{\sqrt{2\pi}U} E_p \quad (1)$$

where

$$E_p = \frac{1}{\sigma_y} \text{Exp}\left(-0.5\left(\frac{y}{\sigma_y}\right)^2\right) \quad (2)$$

¹ All authors are on assignment from National Oceanic Atmospheric Administration, U.S. Department of Commerce.

where U is the dilution wind speed, χ_y is the crosswind integrated concentration, and the term E_p involving the lateral dispersion parameter σ_y is the lateral dispersion model. There are various models available for χ_y , many of which do not rely on Gaussian dispersion in the vertical⁵.

Integrating Equation 1 over a finite line source of length L oriented perpendicular to the wind flow, provides the concentration downwind from a continuous line source emission of $q = Q/L$ mass per unit length per unit time,

$$\chi = \frac{\chi_y}{\sqrt{2\pi U}} E_l \quad (3)$$

where

$$E_l = \frac{2}{\sqrt{2\pi L}} \left\{ \operatorname{erf} \left(\frac{L/2 + y}{\sqrt{2}\sigma_y} \right) + \operatorname{erf} \left(\frac{L/2 - y}{\sqrt{2}\sigma_y} \right) \right\} \quad (4)$$

In Equation 3, E_l is the finite line source lateral dispersion model. As L approaches zero, Equation 4 approaches Equation 2. To avoid inherent limitations in numerical approximations to the erf function, Equation 2 is evaluated wherever the solution to (4) is less than 10^{-6} , and the larger of the two solutions is used.

Lateral Dispersion

For the lateral dispersion parameter, we have chosen a characterization by Briggs⁶ (for rural conditions), that has performed well for point source tracer experiments within the EPA wind tunnel,

$$\sigma_y = \sigma_a x / (1 + 0.0001x)^{1/2} \quad (5)$$

where x is downwind distance in meters and σ_a is 0.08 radians for neutral stability conditions. (The wind tunnel results for building flow simulations are typically scaled 1:250, corresponding to a roughness length of about 4 cm.) Tests were conducted at various downwind distances comparing the lateral dispersion model for a point source release (Equation 2) with the lateral dispersion model for a finite line source release (Equation 4). It was found that Equations 2 and 4 yield numerically identical results at downwind distances of order $100L$. But for all practical purposes, Equations 2 and 4 are quite similar for distances of order $10L$ and beyond.

Finite Line Source Length

Previous characterizations⁷ of wind tunnel experiments of dispersion from surface releases centered on the leeward side of a block shaped buildings have noted that beyond $10H$, where H is building height, the dispersion is that of a point source, having some initial vertical and lateral dispersion. These results when coupled with the similarity of Equations 2 and 4 beyond $10L$, and the patterns of vertically integrated smoke behind various block shaped buildings, suggest that L is of order W , at least for squat buildings with W/H less than 4. The choice of setting L equal to W is consistent with the source configurations used in previous puff simulations¹, where the puff release positions on the leeward side of the building ($W/H = 2$) were spaced along path $1.6H$ in length. Logically, there should be a point when further increase in the width to height ratio would have diminishing affect on the lateral dispersion pattern on an isolated point source at the surface centered on the leeward side of a building. Wind tunnel experiments⁴ suggest that this occurs in the vicinity of W/H of 4. Therefore, we model the length of the finite line source as,

$$L = \begin{cases} W & \text{for } W/H < 4 \\ 4W & \text{for } W/H \geq 4 \end{cases} \quad (6)$$

Crosswind Integrated Concentration

Using results from wind tunnel experiments^{2,4,7}, values for the nondimensional crosswind integrated concentration, C_y , were derived for surface receptors for point source surface releases centered on the leeward side of buildings, where $C_y = \chi_y UH/Q$, where U is at building height. These data are shown in Figure 1 and were summarized as,

$$C_y = a(x/H)^b \quad a = 5(W/H)^{-0.7} \quad b = \frac{\ln(0.45) - \ln(a)}{\ln(100)} \quad (7)$$

The fit of Equation 7 to the data at $x/H = 10$ are shown in Figure 2. It is evident in Figure 2 that beyond $W/H = 12$ Equation 7 tends to underestimate C_y . The observed tendency for C_y to increase for $W/H > 12$ is considered real. As the width to height aspect ratio (W/H) increases, the turbulent eddies induced at the ends of the building have less impact on the initial dispersion behind the building. Characterizing such details in the functional relationship of C_y will have more importance when data become available to substantiate the characterization shown in Figure 1. Dashed lines have been used in Figure 1 to identify regions where there are no data currently available for comparison.

Initial Lateral Dispersion

Previous characterizations of dispersion within the wake of squat buildings^{4,7} suggest that the initial lateral dispersion σ_{y_0} is on the order of $0.7H$. The initial dispersion can be found by solving Equation 5 iteratively for the distance x_0 such that the lateral dispersion equals $0.7H$. The lateral dispersion for any distance downwind is then found using a virtual source model for the lateral dispersion, as $\sigma_y(x+x_0)$.

Results

Substituting Equations 4, 5, 6 and 7 into Equation 3 provides a model for estimating concentrations at surface receptors resulting from dispersion from a ground-level point source centered on the leeward side of a building. The model is for nonreactive, nondepositing releases, with the flow perpendicular to the building. Figure 3 provides a comparison of centerline concentration values for wind tunnel experiments involving a rectangular building ($W/H = 2$, $\sigma_{y_0}/H = 0.7$). The nondimensional concentration C is equal to $\chi UH^2/Q$. In Figure 3, the circles are for wind tunnel tracer experiments⁷ with a 25 cm building height, and the squares are results with a building height of 10 cm.

Figure 4 shows a comparison of the estimated crosswind concentration profile versus wind tunnel results⁷ for the $W/H = 2$ building at $x/H = 3$ and for $x/H = 10$. The solid lines are results using Equation 7. The dashed lines are results using INPUFF¹. Figure 5 shows a comparison at three distances downwind ($x/H = 1.5, 2$, and 5) for wind tunnel experiments involving cubical buildings either 10 or 20 cm on side. Table I summarizes the differences seen in Figures 4 and 5, for receptors near the centerline of the dispersion pattern. For receptors within $x/H = 5$, the finite line source model tends to underestimate the centerline concentration values on average by 10 to 15%.

Conclusions

Further data are needed to provide support and confirmation of the results depicted in Figures 1 and 2, and summarized in Equation 7. The tendency to underestimate slightly the centerline concentrations for the rectangular and cubical buildings for $x/H < 5$ (the cavity region), suggest that some adjustment may be needed either in Equation 7, specification of U , or specification of the initial lateral dispersion σ_{y_0} . Crosswind profile comparisons are needed for buildings with $W/H > 2$, to identify any

dependency of σ_y on building geometry. For the comparisons presented $\sigma_y/H = 0.7$ was used for both the rectangular building ($W/H = 2$) and the cubical building.

The comparisons presented are from wind tunnel experiments which represent neutral stability simulations. In the model presented, atmospheric stability and surface roughness effects have direct influence in the specification of σ_y in Equation 5. We anticipate that within the building cavity and wake region, stability and surface roughness effects will have little influence on C_y (Equation 7). Wind orientation to the building, source location and receptor height will be the most important factors influencing C_y .

It appears, that even if future results were to identify inadequacies in the characterization of the crosswind integrated concentrations provided by Equation 7, we can anticipate that the overall model construct would remain valid. All that would be needed would be an extension of Equation 7 to accommodate the new results. In a similar manner, the characterization of Equation 7 could be extended to receptors at other heights, as data become available.

We speculate that extension of the model for wind orientations other than perpendicular to the building, might be accomplished by viewing the line source as three contiguous line sources, each of length $L/3$. The line source emission rates could be adjusted as a function of wind orientation. Previous results⁴ suggest the largest surface concentrations occur for orientations 45° to the average wind flow. These results also suggest that C_y is a function of source location. Further analysis of data are needed to ascertain the functional dependence of C_y for source location and wind orientation.

Acknowledgements

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Disclaimer

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Table I. Comparison of observed and estimated nondimensional concentrations for receptors within $\pm 0.5H$ of the centerline for the cubical building (Figure 5), and within $\pm H$ of the centerline for the rectangular building (Figure 4)

x/H		Avg. Concentration		Est./Obs.
		Observed	Estimated	
Cubical Block	1.5	18	2.10	1.78
	2.0	24	1.61	1.46
	5.0	42	0.69	0.74
Rectangular Block				
	3.0	23	0.71	0.61
	10.0	30	0.29	0.28

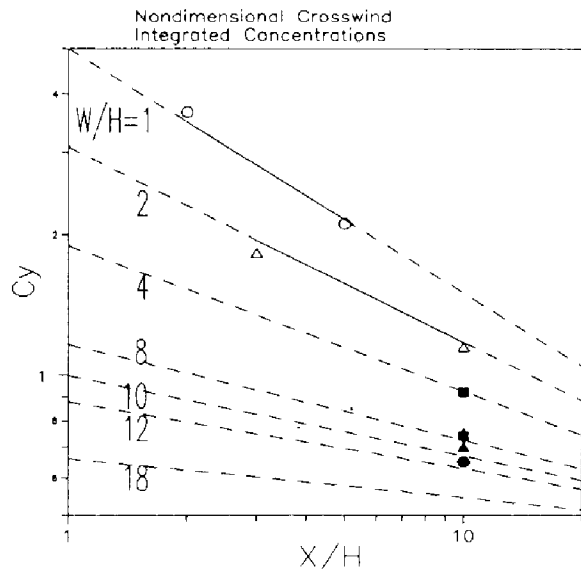


Figure 1. Nondimensional crosswind integrated concentrations for several building width to height ratios (W/H) as a function of scaled downwind distance (x/H). Lines are modeled values given by Equation 7.

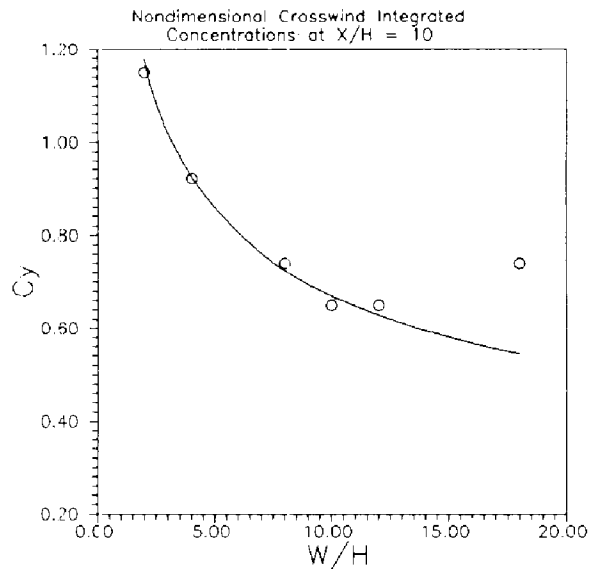


Figure 2. Nondimensional crosswind integrated concentrations for several building width to height ratios (W/H) at scaled downwind distance $x/H = 10$. Solid line is model values given by Equation 7.

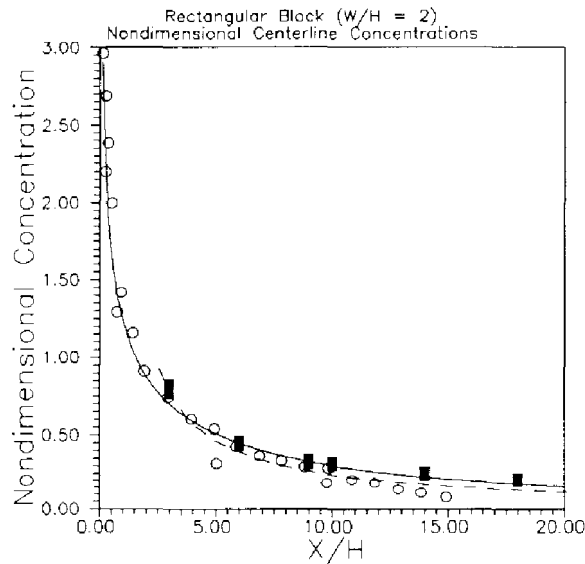


Figure 3. Nondimensional centerline concentrations versus scaled downwind distance for a building width to height ratio $W/H = 2$. Circles and squares are from wind tunnel experiments. Solid line is result using the finite line source model. Dashed line are INPUFF results.

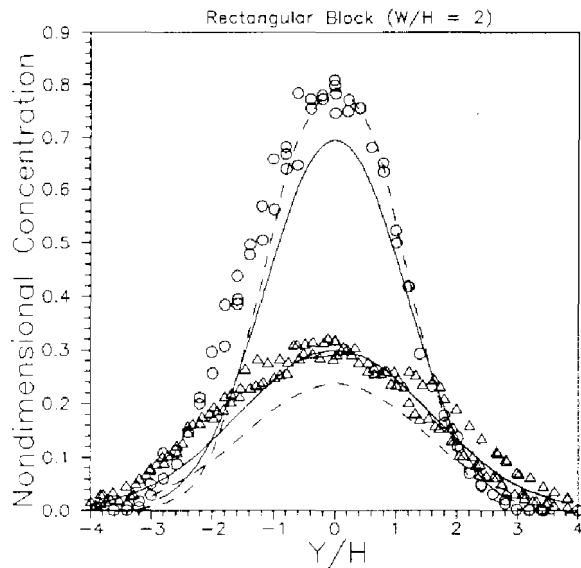


Figure 4. Nondimensional concentrations for a building with a width to height ratio, $W/H = 2$. Wind tunnel results are shown for $x/H = 3$ (circles), and for $x/H = 10$ (triangles). Solid lines are finite line source results, and dashed lines are INPUFF results.

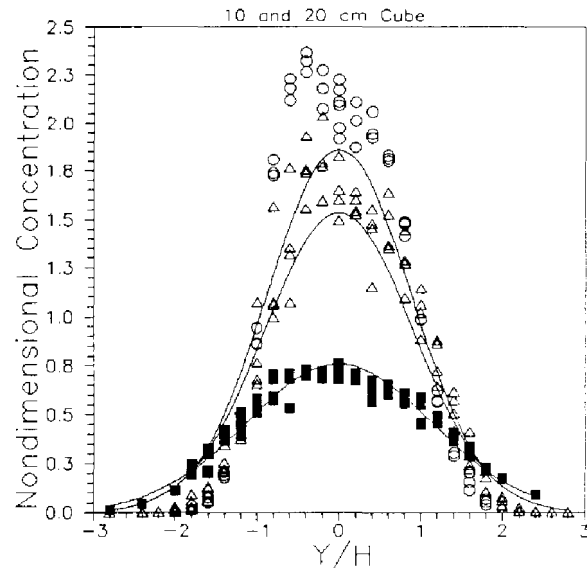


Figure 5. Nondimensional concentrations for a cube. Wind tunnel results are shown for $x/H = 1.5$ (circles), for $x/H = 2$ (triangles), and for $x/H = 5$ (squares). Solid lines are finite line source results.

CONCENTRATION FLUCTUATIONS OF A TOXIC MATERIAL DOWNWIND OF A BUILDING

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Introduction

Investigations of the distribution of pollution in the near-wake region of buildings are needed to better understand the complicated dispersion processes caused by the disturbed air motions near buildings. Concentrations of pollution as emitted into the ambient air are often potentially hazardous. The dilutions of these emissions with the surrounding air naturally reduces the pollution concentrations. The aerodynamic wake flow and thus pollution concentrations are highly dependent on the building shape and length scales, and the approach boundary layer flow. The lateral and vertical mixing initially spreads the pollution over the width and the height of the building. The pollution concentration is also influenced by the downstream extent and the residence time of the recirculating flow adjacent to the building^{1,2}.

Wind-tunnel modeling is a practical method for evaluating building-wake influences. However, the measurement of fluctuating concentrations in wind tunnel studies requires the use of analyzers having a faster response time than is required for full-scale field measurement because of the reduced scaling for wind-tunnel models. There have been some wind-tunnel studies of fluctuating concentrations and new instruments are now available for future studies. Li and Meroney³ evaluated the fluctuation in concentration downwind of a cubical model building. Within one building height downstream of sources on the building, the standard deviations of plume centerline concentrations were found to range from 1 to 3 times the mean concentration. The standard deviation of plume centerline concentrations beyond three building heights downstream was found to be approximately 0.35 times the mean concentration.

A wind-tunnel study^{4,5} of video images of smoke dispersion in the wake of a model building was conducted to provide a measure of the vertically integrated concentration through the plume. These values are well-suited for identifying vortex shedding and horizontal plume meander. A very recent study of video images of smoke flow in the wake of a building has used laser sheet-lighting to provide measures of point concentrations over a horizontal plane⁶. In the following discussion, we used the understanding gained from these wind-tunnel experiments for the development of a puff model for calculating pollutant concentration fluctuations downwind of buildings. A puff model formulation can provide estimates of the average and standard deviation of the concentrations in the building wake. Fluctuations in the spatial-temporal scales of the shed vortices and meander in

¹ Authors are on assignment from National Oceanic Atmospheric Administration, U.S. Department of Commerce.

the plume can be related to the scales of the mean velocity and the building. Here, we compare the cross-stream distribution for a series of video images with the concentration distributions computed with a Gaussian puff model. The model simulations are intended to characterize concentration fluctuations in the wake of a building. Also, averaged concentrations from the puff model were compared with averaged tracer concentrations.

Description of the Wind Tunnel Experiments

The experimental data used in this paper were collected as part of studies conducted in the U.S. Environmental Protection Agency's Meteorological Wind Tunnel. The model building height (H) was either 0.1 m or 0.2 m. The along-stream building length was equal to the building height. The primary case being studied had a building width, W equal to $2H$ which was oriented perpendicular to the direction of the free-stream flow. Data were collected for cases with variation in the building orientation angle and the building width. The mean velocity profile was typical of a neutrally stratified boundary-layer flow. The mean velocity upstream of the building was 2 m/s at an elevation of $0.5H$. An oil-fog smoke was generated and emitted into the wind tunnel through a pipe. The stream of smoke simulated point-source emissions at floor level, midway along the leeward side of the building. Black-and-white video images of smoke were recorded at a rate of 30 pictures per second with a camera connected to a standard VHS recorder. The camera was mounted outside the wind tunnel looking down through a ceiling window. In the first studies, the video luminance analog signal was digitized by a video sequence processor at the North Carolina State University's Image Processing Laboratory. The most recent studies used a collection and digitizing system that was set-up in the EPA Fluid Modeling Facility⁷. The value above the background level is related to the integrated smoke particle density through the field of view. Thus, the original values were corrected by subtracting the estimated background level and then normalized to give a relative measure of concentration. For the experiments under general lighting the normalized scale range should correspond to a unitless scale providing an indirect measure of the smoke concentration integrated vertically through the field of view. For the laser light experiments the values are nearly a point measure (a volume defined by the thickness of the light sheet). Although the relationship between video image intensity and concentration has not been firmly established, we believe the data are useful for the development of a building wake model.

Puff Model Description

The puff model used in this study was INPUFF⁸. INPUFF is a Gaussian Integrated PUFF model that was particularly adaptable to simulating concentrations in the building wake where rapid puff release rates were necessary. Several changes were incorporated into INPUFF to simulate concentrations in the wake of a building: (1) Along-wind dispersion is incorporated into the model, (2) Source position and rate of puff release are a function of building geometry/orientation and wind speed, and (3) The initial sigmas (σ_x , σ_y , and σ_z) are a function of building geometry. Parameters to characterize the puffs were chosen based on the video image analyses. Analysis of the video image data suggested that vortex shedding in the lee of a building can be simulated by puffs that are released at three positions, in sequence along the leeward edge of the building. The source location oscillates between the building edges with a superimposed random component. The first puff is released on the centerline, the second at $-0.8H$, the third on the center, and the fourth at $0.8H$ position. This same pattern repeats for every following cycle except for differences among the random components. The random component is included here for added realism to this model simulation of the measurements. The period of the four puff cycle is computed as follows;

$$P = \frac{14H}{U}$$

where, P is the puff release period,
 H is the building height, and
 U is the wind speed.

For a wind normal to the building the puff release positions are at the center of the leeward edge of the building and $0.8H$ on either side. As the wind direction rotates to a 45 degree orientation the puff release positions are moved along the leeward edge towards the downwind edge. Maximum displacement occurs at a wind direction of 45 degrees. No change is made for wind directions greater than 45 degrees. The video image data was used to develop this empirical relationship but, building orientation effects have not been extensively tested and will be reported in later work. Puffs are always released at the surface. The source strength ($Q=1$ g/s) is distributed so that each of the two puffs released along the building sides contained $Q/3$ and each of the two centerline puffs contained $Q/6$. A random component of $0.2Q$ was also incorporated for added realism.

Virtual source distances are calculated and incorporated into the model so that at the leeward edge of the building the dispersion parameters (σ_x , σ_y , and σ_z) were set equal to;

$$\frac{\sigma_z}{H} = 0.7 + 0.0625 \left(\frac{W}{H} - 2 \right) \quad \text{for } \frac{W}{H} \leq 10 \qquad \frac{\sigma_z}{H} = 1.2 \quad \text{for } \frac{W}{H} > 10$$

$$\frac{\sigma_y}{H} = 0.35 \frac{W}{H} - 0.0625 \left(\frac{W}{H} - 2 \right) \quad \text{for } \frac{W}{H} \leq 10 \qquad \frac{\sigma_y}{H} = 0.3 \frac{W}{H} - 0.35 \left(\frac{W}{H} - 10 \right) \quad \text{for } 10 \leq \frac{W}{H} \leq 30$$

$$\sigma_x = 1.5\sigma_z$$

In the puff simulations of dispersion, P-G stability class "D" was used to characterize the rate of growth of the puffs. σ_x and σ_y were assumed to have the same growth rate.

Results

We have been investigating the performance of the modifications made to the puff model. The above section presents the parameters as they were used in the analyses reported here. There is a very delicate 'play' between the choice for the period, the size of σ_x relative to σ_z , and the degree of randomness that is included in the model. The degree of fluctuation is very sensitive to the selected combination of these parameters. The selected parameters used here are consistent with the general observations made of the smoke prior to these model simulations.

Figure 1 compares the cross-stream profile of mean values across the plume at $x/H=3$. The video image data and the model estimates have been normalized to match the tracer value at $y/H=0$. Once normalized, the spatial and temporal distributions of the video data should be a valid measurement. The model and tracer concentrations are non-dimensionalized by UH^2/Q ; where U is the approach velocity at $z=H$, H is the building height, and Q is the emission rate. Since the source is located near the building where the mean wind is reduced in comparison to the free stream approach flow, some compensation for this effect must be made in the model concentration estimates. The model input includes a puff advective velocity which applies fully to the effective plume dilution at some distance downwind of the building (e.g. $x/H=15$). Thus, to compare with wind tunnel tracer concentrations which actually feel this reduced wind, a modified model velocity is used. The adjusted velocity used in these comparisons was fixed to equal the reduced velocity in the wind tunnel.

$$\frac{U_{(atH)}}{U_{(modified)}} = 0.95 + 6.42 \left(\frac{x}{H} \right)^{-1.77} \quad \text{for } 3 < x/H < 15$$

Figure 2 compares the model and tracer cross-stream profiles at $x/H=10$; there are no video data at this downstream distance. Figure 3 compares the model and tracer concentrations along the centerline. The comparison at distances beyond $x/H=10$ could be improved by incorporating dispersion parameters specific to conditions found in the wind tunnel in place of the P-G dispersion parameters. These figures show that the mean profiles for the puff model compare well to measurements.

We are interested in seeing how well the puff model can characterize fluctuating concentrations in the building wake. The cross-stream distributions of several statistics for the time series of video image and model data were compared. The video image values and the model values were normalized by the mean centerline value. Figure 4 compares the profiles for the value of the standard deviation divided by the mean centerline value for the series. The standard deviations for the model lie between the laser and general light values from the video images. Figure 5 presents example time series values at $y/H=0$ at $x/H=3$. Similar comparisons are observed at other cross-stream positions. Time has been normalized by the observed period of oscillation (0.64 s for video, 18 s for INPUFF). The temporal resolution of the video values is 19 per cycle while for INPUFF it is 18 per cycle. The model values (5a) compares best to the video values for the general light (5c). The spatially integrated concentration for the general light video values is in effect similar to a temporal average over a shed vortex in the building wake flow and thus should be comparable with that modeled by an advected puff. The video values for the laser sheet-lighting should represent short-term (on the order of 30 second) averaged field values.

Conclusions and Recommendations

The puff model simulates many features of the larger scale variation observed in the building wake flow but does not simulate the short term peaks. This could be overcome by adding an empirically determined factor for the relative short term peaks. However, this feature would not be necessary for most applications where average concentrations over several minutes are needed. These comparisons indicate that a 4 puff per cycle model can be used to simulate the overall characteristics of building-wake dispersion. The puff model also has the special feature of being able to simulate the effects of meander and rapidly changing conditions for emissions and meteorology. The building wake formulations developed in the puff model are based on analysis of the video image data from wind tunnel studies and are considered preliminary.

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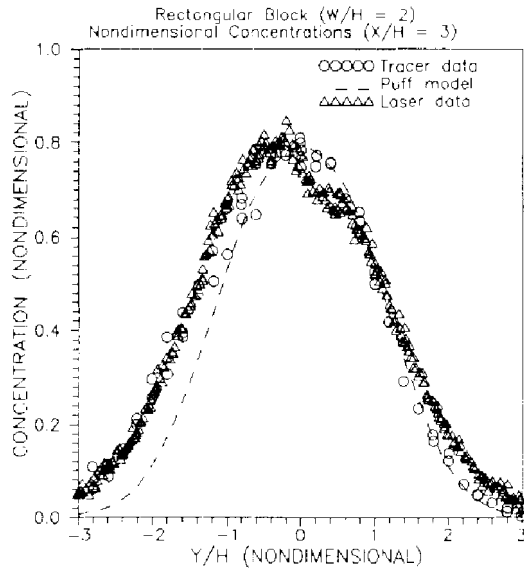


Figure 1. Nondimensional lateral concentration at 3 building heights downwind.

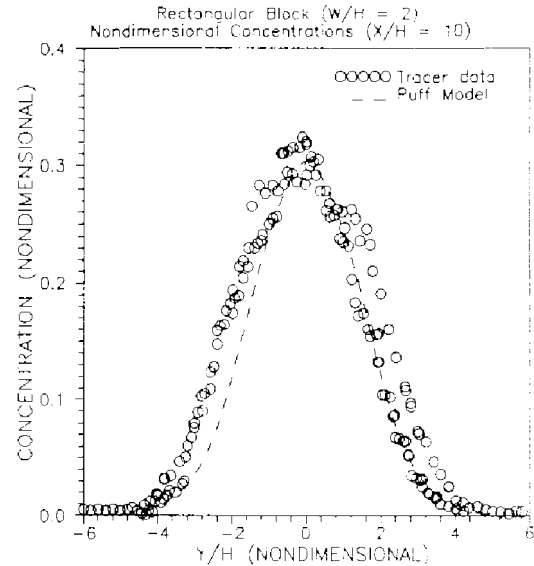


Figure 2. Nondimensional lateral concentration at 10 building heights downwind.

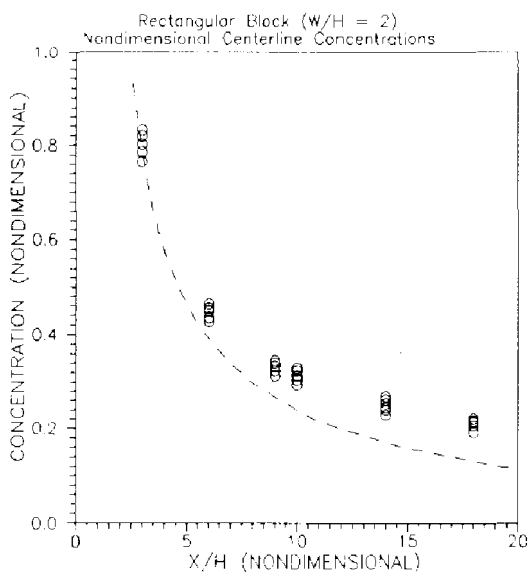


Figure 3. Nondimensional centerline concentration for tracer data (circles) and model results (dashed line).

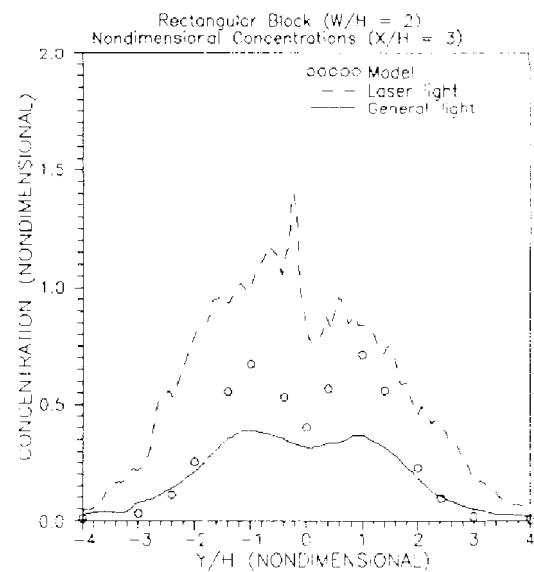


Figure 4. Standard deviation of nondimensional lateral concentration at 3 building heights downwind.

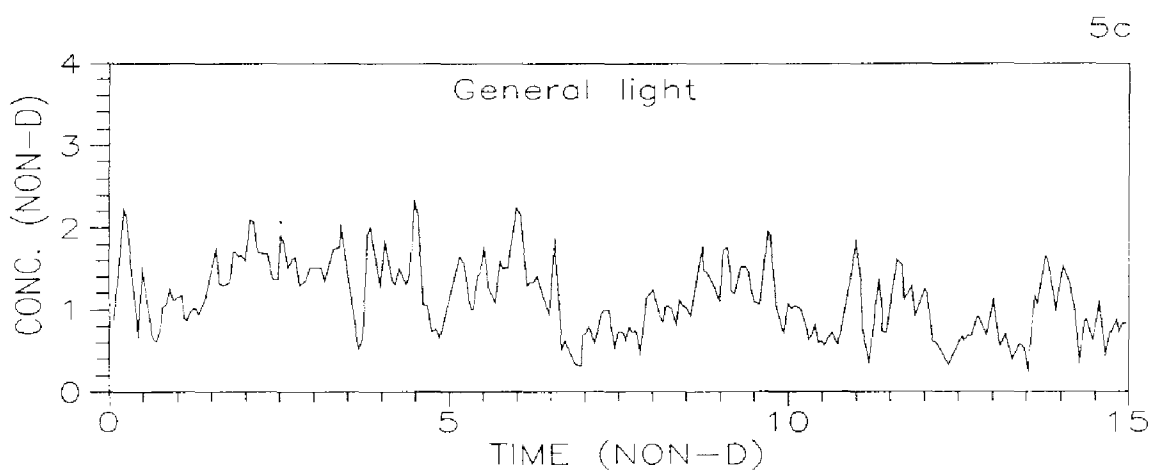
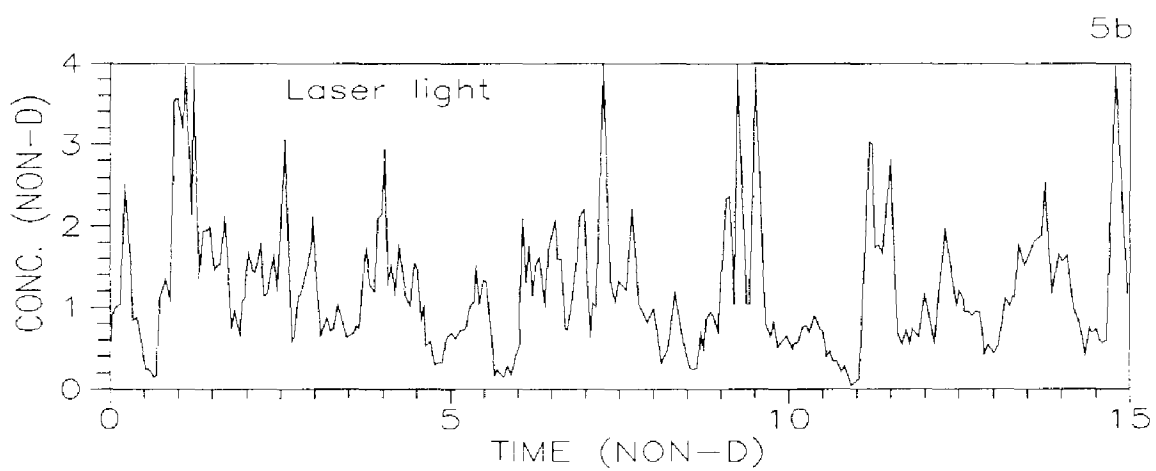
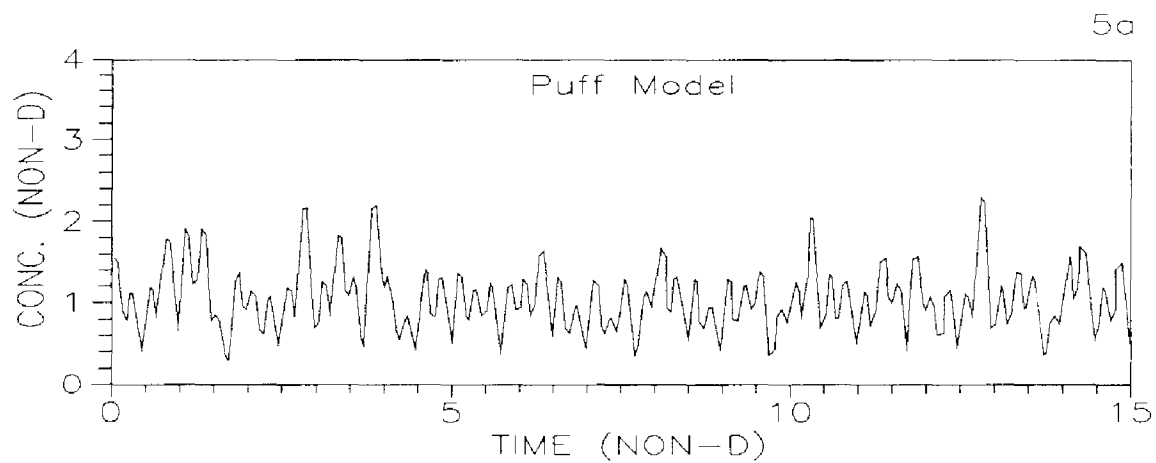


Figure 5. Concentration versus time at $y/h=0$ three building heights downwind.

HAZARDOUS WASTE INCINERATOR

EVALUATION PROGRAM

BY

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INTRODUCTION

The disposal of hazardous wastes in a safe manner has been a concern since the 1970's. Indiscriminate dumping of chemical wastes of all types had been going on since the birth of chemical industries in the U.S. Methods of disposal, such as incineration, that would have eliminated wastes permanently, were initially disregarded as being too costly. However, many of the major companies installed incinerator facilities on their own plant sites; not because it was the most economical method but because they realized that other methods of disposal would not be open to them. It is estimated that a total of 100 million tons of organic chemicals wastes are generated in the U.S. every year and only 5% of these wastes are treated through incineration. Under the amendments to the Resource Conservation and Recovery Act (RCRA) that were passed in 1985, the Environmental Protection Agency (EPA) is required to ban the land disposal of many hazardous wastes unless it can be proved that such wastes can be safely disposed of to the land. As a result, incineration as a means of hazardous waste disposal, especially for organic materials, is becoming popular.

The ultimate goal of hazardous waste incineration is to destroy the waste material with as high a destruction efficiency as possible. Under the RCRA, every incinerator should show that it can adequately destroy those hazardous waste constituents which are most difficult to incinerate. In general, the governing regulatory agency will select compounds within the inlet mixture which are of sufficient toxicity, concentration, and thermal stability so as to be designated as principal organic hazardous constituents (POHCS). During the incineration of hazardous wastes, compounds not identified in the waste feed may be formed. These compounds are known as products of incomplete combustion (PICS). In order to obtain an operating permit for a hazardous waste incinerator, it must be shown by trial burn that the incinerator meets or exceeds the following performance standards:

- 99.99% Destruction Efficiency
- 0.08 gr/dscf of particulate emissions corrected to 7% oxygen

- 4 lb/hr of hydrogen chloride emissions or a 99% removal efficiency

This paper describes the experimental program undertaken to evaluate the performance of two large hazardous waste in-plant incinerators used in converting liquid and gaseous chlorinated hydrocarbons into hydrochloric acid product. The sample collection methods, analytical techniques employed, quality assurance and quality control program instituted along with results are described in this paper. In particular, this paper discusses the details of dioxin/furan testing results.

PROCESS DESCRIPTION

The waste gases and liquids from the process area of a chemical plant are fed to two oxidation units that convert chlorinated hydrocarbons into hydrochloric acid, by passing through an absorption system. Then the exhaust gases are vented to the atmosphere. The major components that are fed to the oxidation units are provided in Table 1. It was expected that these incinerators do not produce any hazardous toxic compounds.

SAMPLING METHODOLOGIES

The sampling program, recovery, and analytical methodologies were designed during this program to ensure:

- Collection of a representative sample;
- Minimization of both sample loss in the train and contamination by sampling train components;
- Quantitative recovery of the sample from all parts of the train; and
- Appropriate sample pretreatment to achieve quantitative extraction, concentration, and negligible interferences during analysis.

Before designing the protocol, it is important to identify the key organic components that are exhausted from the process, by considering key POHCs. Table 2 provides a typical list of POHCs and corresponding PICs.

The designated POHCs during this program were chosen by considering:

- Concentration of organics in the feed
- The rank of incinerability.

In addition, a whole range of PICs were also considered.

The following documents were used to develop the sampling and analytical methodologies for this program:

- ASME/EPA Draft Protocols for the Determination of Chlorinated Organic Compounds in Stack Emissions [1, 2, 3]
- Battelle Laboratory Procedure for Sampling and Analysis of Polynuclear Aromatic Hydrocarbons [4]

- Protocol for the Collection and Analysis of Volatile POHC's (Principle Organic Hazardous Constituents) using VOST (Volatile Organic Sampling Train) [5]
- Texas State Department of Health - Compliance Manual for the Measurement of Chlorine and Hydrogen Chloride [6]

TABLE 1: MAJOR COMPOUNDS THAT ARE FED TO INCINERATORS

Chloroethene/Vinyl Chloride
 1, 2 - dichloroethylene
 Dichloroisopropyl Ether
 Dichloropropanol
 Epichlorohydrin
 Ethylene Dichloride
 Hexachlorobenzene
 Hexachlorobutadiene
 Hexachloroethane
 Hexachlorobutylene
 Hexachloropropane
 Octachlorostyrene
 Pentachlorobutylenes
 Propylene Chlorohydrin Ethane
 Propylene Dichloride
 Propylene Oxide/Propionaldehyde Acetone
 1, 1, 2, 2 - tetrachloroethane
 Tetrachloromethane
 1, 2, 3 - trichlorobutylene
 1, 1, 2 - trichloroethane

TABLE 2: TYPICAL POHCs AND CORRESPONDING PICs (8)

Designated POHC	Products of Incomplete Combustion
Carbon Tetrachloride	Tetrachloroethylene Hexachloroethane
Chloroform	Tetrachloroethylene Carbon Tetrachloride
Chlorobenzene	Benzene
Toluene	Benzene
Trichlorobenzene	Chlorobenzene Dichlorobenzenes
Ketone	Hexachlorobenzene
Pentachloroethane	Tetrachloroethylene
PCBs	Chlorinated dibenzofurans

- EPA Stationary Source Sampling Methods for the Determination of Total Hydrocarbons and Vinyl Chloride [7]

Table 3 provides a list of sampling methods used during this program. All procedures employed here were in accordance with USEPA recommended methods.

TABLE 3: SAMPLING METHODS EMPLOYED DURING THIS PROGRAM

Type	General Compounds of Interest	Sampling Method
Most volatile B.P. < 30°C	Vinyl Chloride	EPA Method 18
Volatile B.P. (30° - 100°C)	Methylene chloride	VOST
Semi-volatile B.P. (100° - 200°)	Chlorobenzenes	Modified Method 5
Non-volatile B.P. > 200°C	Dioxins/Furans	Modified Method 5
Acids	Hydrochloric acid	Texas Method
Gases	Chlorine	Texas Method

PREPARATION OF SAMPLING TRAIN

All recommended procedures including proving (1) were employed for the preparation of sampling trains. The quality of the pretest cleanup for organics sampling is crucial, due to the expected low concentration of heavy molecular weight organics. Hence, cleaning and proving protocols for trains were strictly followed to ensure that contaminants from sampling equipment would not interfere with the analysis. The protocols include:

- Rinsing all glassware and train components with solvents such as methanol, acetone and methylene chloride
- Final washing with pentane
- Sealing precleaned glasswares with proven aluminum foil
- Soxhlet extraction and proving tenax and XAD-2 sorbent cartridges using ASME protocol (1)

The proving of the trains was performed by concentrating and analyzing the final pentane extract using the analytical methodologies illustrated in the later section of the paper. The total allowable background concentration of chlorinated organics was limited to 100ng per train (includes all train components). If the analysis of proving extract indicated a higher level, all train components were once again subjected to the same cleaning process, before using for sampling.

ON-SITE SAMPLING AND SAMPLE RECOVERY

All sampling was conducted by personnel experienced with test procedures and cognizant of the analytical techniques for trace organics, particularly contamination problems. A total of 8 tests were conducted to identify variability on emission rates.

Extreme care was exercised during the sampling of heavy molecular weight organics (semi and non-volatiles). A new set of train components was used for each test. The various components of the sampling train were leak checked separately prior to assembly. A total vacuum of 15 inches Hg or higher was drawn and maintained for 2 minutes. If a leakage rate was found to be 0.02 CFM or greater, the specific assembly was dismantled and reassembled until the leak was adequately reduced or eliminated completely. This step wise procedure was followed consistently to identify the location of leaks in separate components. Finally the entire train, including the probe, was checked accordingly, prior to the start of sampling. Leak checks were performed before and after each traverse of a test.

Actual sampling time of three hours was necessary in all tests to collect a minimum of 80 to 120 cubic feet of stack gas for each test. Isokinetic sampling was achieved through the use of appropriate pre-test data to develop the isokinetic sampling rate equation needed to predict the pressure drop across the sampling train orifice for each velocity pressure measured.

At the end of each test, the pump was turned off and post-test leak checks were completed before transporting the probe-impinger assembly to the on-site laboratory. A blank train was set up in the same manner as actual test trains for the entire duration of each test with no sample collection. This provided quantitative residual contamination that could occur under site conditions.

The VOST and hydrocarbon sampling were conducted in accordance with the respective protocols. All required, trip, field and laboratory blanks were used in accordance with the protocol.

Quantitative recovery of heavy molecular weight samples from all parts of the train required a rigorous and meticulous procedure. In order to avoid any contamination, the stack sampling train assembly was transported to the on-site laboratory for partial sample recovery. The samples were recovered in a fashion to provide catches for the analyses of chlorinated and polynuclear aromatic hydrocarbons (heavy molecular weight organics). The following samples were collected from each train:

- nozzle, probe and front half of the filter
- filter
- condenser and back end of the filter
- sorbent tube
- impinger 1
- impingers 2 and 3

All train components were washed with respective solvents as specified in the protocol followed by pentane wash. This final wash was separately analyzed in each test to provide a quantitative recovery efficiency.

ANALYSIS AND QUALITY CONTROL

The samples collected from the field during the dioxin/furan testing program were analyzed as individual catches for heavy molecular weight organics by employing standard methods. This method of analysis provided details of the various organics that were collected in various parts

of the train. Figure 1 illustrates the schematics of the procedures adopted prior to analysis. Table 4 lists appropriate surrogates and internal standards used during this program. These were added in the following manner before the extraction procedure was begun:

20 ml of BNA surrogate
200 ml of PCB surrogate
200 ml of dioxin internal standard/surrogate

The extracts to be analyzed for dioxin/furans were cleaned up using the combination base/acid silica gel as described in the ASME protocol [2]. These were also cleaned using the basic alumina column described in the ASME protocol [2]. The eluent from the column was then concentrated to 50 ul before subjecting it to analysis.

The analysis of these extracts were performed for:

- dioxins/furans (including members of dirty dozen family as described in Table 4) and other tetra to octa congener groups
- PCBs (all congener groups)
- Polynuclear Aromatic Hydrocarbons
- Chlorobenzenes
- Chloroethanes
- Octachlorostyrenes

using gas chromatography/mass spectrometry.

The quality control/quality assurance program for the dioxin/furan analysis involved:

- analysis of samples spiked with stable isotopically labelled internal standards listed in Table 5;
- processing and analysis of one blank sample with each extraction batch;
- matrix spike duplicate (MSD) pair of analysis with each extraction batch;
- analysis of glassware rinses collected prior to usage of the trains;
- analysis of glassware rinses collected after usage of the trains;
- analysis of distilled, deionized water used in the preparation of the trains;
- analysis of catches collected from the various components of the field blank trains; and
- splitting of selected samples for analysis by Regulatory Agency Laboratory.

RESULTS AND DISCUSSION

Tables 5, 6, 7 and 8 provide the testing results of this program. Because of the complex nature of the program, only the important results are provided in this paper. The numbers indicated in parentheses were positively identified, whereas the other numbers represent the limit of detection of individual compounds based on sample volume, extraction procedure, and analytical method used. The testing program revealed that:

- only total penta-furan and octa-dioxin congeners were found in the exhaust stream;
- no members of the dirty dozen family were positively identified;
- hexachlorobutadiene and hexachlorobenzene were identified positively;
- many of the volatile organics fed to the incinerators were identified positively;
- no vinyl chloride monomers were detected positively;
- excellent recoveries of surrogates from matrix spike and matrix spike duplicate samples were obtained (Table 9);
- no significant contamination of the blank train was observed (Table 10);
- presence of naphthalene was observed in the sorbent trap in all tests;
- compounds with higher chlorination produced lower destruction efficiencies; and
- an analysis of variance of spiked compound recoveries showed the mean percent recoveries were equal at a level of significance less than 0.005.

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FIGURE 1: SCHEMATICS OF LABORATORY PROCEDURES ADOPTED FOR HEAVY MOLECULAR WEIGHT ORGANIC ANALYSIS

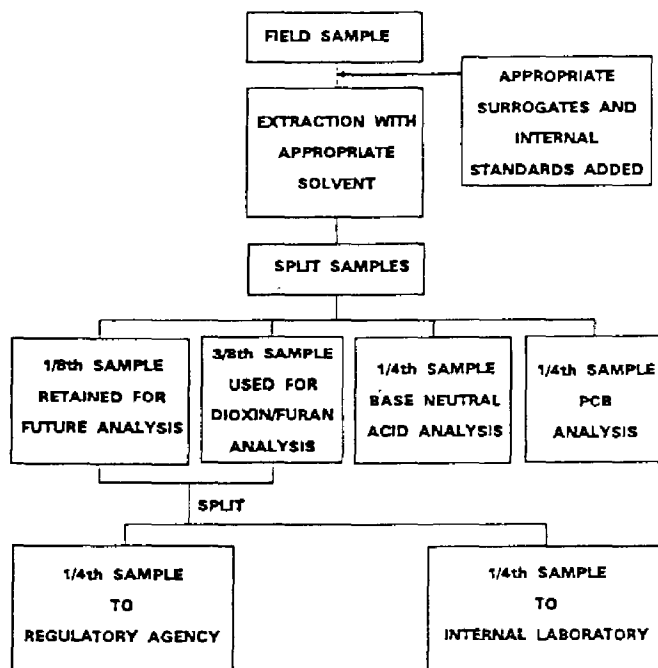


TABLE 4: INTERNAL STANDARDS AND SURROGATES ADDED TO FIELD SAMPLES

SURROGATE COMPOUNDS

COMPOUND	ANALYSIS
¹³ C-4,4'-DDT	Polychlorinated Biphenyls
³⁷ Cl-2,3,7,8-TCDD	Dioxin/Furan
D ₅ -nitrobenzene	Base Neutral Acid
2-fluorobiphenyl	Base Neutral Acid
D ₁₄ -terphenyl	Base Neutral Acid
2-fluorophenol	Base Neutral Acid
D ₅ -phenol	Base Neutral Acid
2,4,6-tribromophenol	Base Neutral Acid

INTERNAL STANDARD COMPOUNDS

COMPOUND	ANALYSIS
¹³ C-2,3,7,8-TCDD	Tetrachlorodioxins and furans
¹³ C-1,2,3,7,8-PCDD	Pentachlorodioxins and furans
¹³ C-1,2,3,6,7,8-HCDD	Hexachlorodioxins and furans
¹³ C-1,2,3,4,6,7,8-H ₇ CDD	Heptachlorodioxins and furans
¹³ C-1,2,3,4,6,7,8,9-OCDD	Octachlorodioxins and furans

TABLE 5: RESULTS OF DIOXIN/FURAN ANALYSIS

Compound	Concentration, ng/m ³		Blank Train ng
	Low	High	
Total Tetra-Dioxin	0.5	3.0	0.4
Total Tetra-Furan	0.7	2.2	0.4
Total Penta-Dioxin	2.8	4.3	1.7
Total Penta-Furan	1.3	[5.3]	1.0
Total Hexa-Dioxin	1.3	12.0	0.3
Total Hexa-Furan	1.7	6.5	0.3
Total Hepta-Dioxin	2.3	4.9	0.6
Total Hepta-Furan	1.0	2.2	0.3
Total Octa-Dioxin	1.7	[9.4]	1.3
Total Octa-Furan	1.7	4.5	0.5

[] Positive Identification

TABLE 6: RESULTS OF BASE NEUTRAL/ACID COMPOUND ANALYSIS

Compound	Concentration, ug/m ³		Blank Train ug
	Low	High	
Trichlorobenzene	5.0	7.3	20
Tetrachlorobenzene	23	32	90
Trichlorophenol	15	22	60
Pentachlorophenol	23	33	90
Hexachloroethane	15	27	60
Hexachlorobutadiene	[6.2]	[10]	80
Hexachlorobenzene	[6.2]	[7.8]	90
Octachlorostyrene	64	112	250
Pentachlorobenzene	25	45	100
Pentachloroethane	26	36	100

[] Positive Identification

TABLE 7: RESULTS OF VOLATILE ORGANICS

Compound	Concentration, ppm
Chloroform	0.009 ± 0.003
Trichloethane	0.028 ± 0.015
Trichloethylene	0.002 ± 0.001
Tetrachloethylene	0.066 ± 0.012
1,2-dichloroethane	0.014 ± 0.009
Vinyl chloride	< 0.5
Propylene dichloride	0.0008 ± 0.0002

TABLE 8: RESULTS OF DIRTY DOZEN DIOXINS/FURANS

Isomer	Concentration, ng/m ³	
	Low	High
2,3,7,8 - TCDD	0.1	3.0
2,3,7,8 - TCDF	0.1	2.0
1,2,3,7,8 - PCDD	1.4	2.2
1,2,3,7,8 - PCDF	0.7	2.0
1,2,3,4,7,8 - H _x CDD	0.4	3.2
1,2,3,4,7,8 - H _x CDF	0.4	3.0
1,2,3,7,8,9 - H _x CDD	0.3	4.1
1,2,3,7,8,9 - H _x CDF	0.1	3.1
1,2,3,6,7,8 - H _x CDD	0.2	3.2
1,2,3,6,7,8 - H _x CDF	0.2	3.1
1,2,3,4,6,7,8 - H _p CDD	0.3	2.1
1,2,3,4,6,7,8 - H _p CDF	0.3	0.9

Note: All values represent instrumental limit of detection and none of the compounds were positively identified.

TABLE 9: TYPICAL MATRIX SPIKE RESULTS - IMPINGER SAMPLES

Compound	Parameter	Matrix Spike	Matrix Spike Duplicate
TCDD	Amt. Spiked	7.5	7.5
	Amt. Recvd	7.80	7.79
	% Recovery	104.00	103.91
PCDD	Amt. Spiked	15	15
	Amt. Recvd	14.875	15.519
	% Recovery	99.17	103.46
HCDD	Amt. Spiked	15	15
	Amt. Recvd	16.482	15.602
	% Recovery	109.88	104.01
H7DD	Amt. Spiked	7.5	7.5
	Amt. Recvd	7.771	7.599
	% Recovery	103.61	101.32
OCDD	Amt. Spiked	7.5	7.5
	Amt. Recvd	9.381	9.296
	% Recovery	125.08	123.95
OCDF	Amt. Spiked	15	7.5
	Amt. Recvd	16.948	17.978
	% Recovery	225.97	239.71

Note: All amounts spiked were in nanograms.

TABLE 10: RESULTS OF DIOXIN ANALYSIS FROM A TYPICAL BLANK TRAIN

Compound	Probe & Nozzle (ng)	Filter (ng)	Condenser (ng)	Sorbent Tube (ng)	Impinger #1 (ng)	Total ng
Total						
Tetra-Dioxin	<0.1	<0.3	<0.2	<0.7	<0.4	<1.8
Total						
Penta-Dioxin	<0.7	<7.9	<1.1	<7.4	<1.9	<1.9
Total						
Hexa-Dioxin	<0.4	<10	<0.5	<1.3	<0.6	<25
Total						
Hepta-Dioxin	<0.8	<2.5	<1.1	<5.4	<0.4	<10
Total						
Octa-Dioxin	<1.2	<7.6	<2.0	<18	<1.3	<30

Remote Optical Sensing of VOCs: Application to Superfund Activities

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INTRODUCTION

Ambient air monitoring is conducted for a variety of purposes under the Comprehensive Environmental Response, Compensation and Liability Act of 1980 (CERCLA or "Superfund"), as amended by the Superfund Amendments and Reauthorization Act of 1986 (SARA). Remote optical sensing can be an ideal method for assessing the air migration pathway for many activities spanning the Superfund process. However, proper application of this emerging technology requires a clear understanding of its uses and limitations, as well as definition of appropriate data quality objectives (DQOs) for each activity. DQOs are defined as the qualitative and quantitative statements that specify the quality of data required to support a decision-maker's needs.¹² In this context, DQOs include ambient air monitoring program objectives and the data quality needs necessary to ensure their achievement.

This paper is directed toward environmental managers responsible for the design and implementation of Superfund-type ambient air quality monitoring investigations. DQOs are identified for a variety of air-related Superfund activities for which application of this technology is appropriate. Suggested monitoring approaches and methodologies for achieving each DQO are presented. Finally, limitations are discussed for the above applications.

OVERVIEW OF MONITORING TECHNIQUE

Remote sensing is generally defined as the ability to detect an object or phenomenon without having the detector in direct contact with the object being detected. This technique can be either passive where some natural source of radiation is received, as in the case of a satellite that maps infrared (IR) emissions from the earth's surface, or active where the sensing system probes the object of measurement in some way and infers the parameter being measured from the object's response, as in the case of radar. Remote sensing, as applied to air toxics measurements, is an active

optical technique that involves the use of long-path spectroscopy. Long-path spectroscopy has been used in a wide variety of environmental applications during the past 15 years.³⁻⁹ The basic principle involves the generation and propagation of light in a known wavelength, or range of wavelengths, and the subsequent detection and spectral analysis after some pathlength has been traversed. By creating a ratio between the detected signal and the emitted signal and comparing this ratio to a library of known absorption spectra, individual species can be identified and quantified. Certain compounds are observed principally in the IR, other compounds are observed principally in the ultraviolet (UV), and still others are observed equally well in either.

A fundamental difference between remote optical sensing and traditional point-sampling techniques involves the nature of the data output. This difference must be clearly understood by those who interpret and apply remote sensing data. As will be shown later, the key to the tremendous advantages offered by remote optical sensing for Superfund application lies in the nature of its data output. For point-sampling techniques, gaseous contaminant concentrations are generally reported either in mass of contaminant per unit volume of gas, such as micrograms per cubic meter ($\mu\text{g}/\text{m}^3$), or in volume of contaminant per volume of gas, such as parts per million (ppm) or parts per billion (ppb). Open-path remote sensing, however, is a volume-averaging technique where total contaminant burden is measured within a cylinder defined by the finite cross-section of the light beam at each end and the length of the beam itself. This volume average is reported as a path-integrated concentration typically normalized to a pathlength of 1 meter. If, for example, an integrated concentration of 30 ppm-m is reported, no information concerning the contaminant distribution can be directly inferred, and the instrument response would be identical whether there was a uniform concentration of 30 ppm over a distance of 1 meter, 3 ppm over a distance of 10 meters, 300 ppb over a distance of 100 meters, or 3 ppb over a distance of 1 kilometer.

DATA QUALITY NEEDS

Ambient air quality monitoring programs conducted under Superfund are frequently designed and implemented without adequate understanding of the decisions to be made based on the data. Data collected during programs employing traditional point-sampling techniques at complex hazardous waste sites rarely have been of a quality and quantity sufficient to achieve the DQOs required in meeting a decision-maker's needs.

The principal deficiencies associated with data collected via traditional point-sampling techniques involve data representativeness and comparability. The complex nature of air dispersion, combined with the spatial variability of air emissions typical of Superfund sites, has made it difficult, and often impossible, to use point-sampling techniques to identify and characterize contaminant plumes for subsequent assessment of long-term downwind air impacts. Compounding this problem of data representativeness is an increasing need to generate real-time data for a variety of health-related assessments. On-site and off-site health and safety concerns during site remediation and emergency response activities frequently dictate the need for continuous real-time assessment of contaminant emissions and ambient air concentrations.

Data comparability has historically been a problem for point-sampling techniques because of an inability to collect data with identical meteorological conditions throughout the sampling period. This, combined with a lack of adequate documentation of atmospheric transport conditions, has made it virtually impossible to produce air monitoring data that are comparable when collected over sequential stages of the Superfund process.

A carefully designed air monitoring program involving remote optical sensing, together with complementary traditional point sampling and on-site meteorological monitoring, can surmount these problems and produce statistically valid, volume-averaged measurements over long distances (pathlengths) in near real time (less than 15 minutes). The statistical representativeness intrinsic to path-integrated air measurement data ensures its comparability throughout the Superfund process.

SUPERFUND APPLICATIONS AND MONITORING METHODOLOGIES

Table 1 summarizes Superfund activities for which application of remote sensing is appropriate, and presents corresponding DQOs. Three main types of Superfund activities are identified: site assessment, remedial, and emergency response. Within each of these types, specific activities are identified along with their corresponding DQOs. It must be kept in mind that remote sensing may not be suitable to meet all air monitoring needs, as migration of contaminated particulate matter cannot be assessed via this technique. Following is a discussion of each Superfund application and corresponding DQO.

Site Assessment Applications

HRS Model Scoring

Hazard Ranking System Model (HRS) scoring is performed to assess the relative degree of risk posed by known or suspected uncontrolled hazardous waste sites, thereby providing a uniform basis for site placement on the National Priorities List (NPL) for cleanup. Separate scores are calculated for each contaminant migratory pathway. A score for the air route is calculated based either on a demonstrated "observed release" or on the demonstrated potential for an observed release. Demonstration of an observed release is preferable, and generally requires air measurement data showing detectable concentrations off site in the downwind direction together with appropriate documentation supporting the contention that the site is the source. The HRS Model does not attempt to relate a non-detect to some maximum level of risk.

The DQO for HRS Model scoring is to conclusively demonstrate the presence or absence of off-site migration of air contaminants. Remote optical sensing is ideally suited to achieve this DQO if the plume is non-buoyant and originates from a ground-level source (i.e., the plume hugs the ground as it travels downwind from the source). This is a good assumption for most hazardous waste sites, as gaseous contaminant releases are generally the result of volatilization from impoundments or hazardous waste storage areas. Emissions from such sources can be detected if the long-path beam is shone along the site perimeter, downwind of the suspected source area and across the plume. If contaminants are detected, upwind monitoring would then be

conducted along the upwind site perimeter to demonstrate that the contaminants detected downwind are attributable to the site and are not being advected across the site from some upwind source. Because air monitoring for HRS Model scoring is typically a one-time event, it is important that it be conducted under meteorological conditions representative of reasonable worst-case emissions and transport.

Remedial Applications

RI Air Monitoring

Remedial investigations (RIs) are conducted in conjunction with feasibility studies (FSs) to assess the nature and extent of contamination at NPL sites. This information is used to support the detailed engineering evaluation of all technically feasible remedial alternatives and to provide a baseline against which the effectiveness of each alternative, including the no-action alternative, can be assessed. Because air emissions are a "secondary" effect, indicative of the presence of waste products or contaminated soils or water, air monitoring data are not appropriate to support remedial engineering decisions. Instead, air monitoring data generated during the RI are typically used as a baseline against which the effectiveness of each remedial alternative is assessed, and to support the appropriateness of the no-action alternative.

The DQO for RI air monitoring is to provide air contaminant data suitable for generation of accurate emission rate estimates under undisturbed conditions. These emission rates can then be compared to those predicted to occur following implementation of various remedial actions, and can also be used as input into air quality dispersion models to evaluate downwind community health impacts in support of evaluation of the no-action alternative.

Remote optical sensing is one of only a few techniques available to measure emission rates for RI baseline emission estimates. For large sites with complex sources of air emissions, remote sensing may be the only technique that is not cost-prohibitive. Path-integrated concentrations measured at known downwind distances, together with on-site meteorology, are used to satisfy basic relationships derived from classical Gaussian dispersion theory¹⁰ which lead directly to quantification of source emission rates.¹¹ The measurement technique requires minimal understanding of site characteristics, and the resultant emission rates can be easily calculated in the field. It is important that both upwind and downwind measurements be made so that issues of source apportionment are resolved.

FS Air Monitoring

Air is the only media in which the exposure potential drastically increases during site cleanups. Because many Superfund sites are very close to downwind populations that could be affected by these emissions, it is becoming more common for pilot studies to be conducted during either the feasibility study or the remedial design itself. Pilot studies simulate, on a small scale, the ultimate cleanup in order that emission rates for the contaminants can be determined for each of the cleanup steps. These emission rates can then be modeled in order to estimate the downwind health impacts associated with that cleanup option and to determine the necessary degree of emission controls.

The DQO for FS air monitoring is to provide air contaminant data suitable for generation of accurate emission rate estimates during pilot-scale assessments of cleanup alternatives. Remote optical sensing can be used to meet this DQO in a manner identical to that described for obtaining baseline emissions during the RI. Once downwind exposures are quantified, the suitability of various emission controls can be easily evaluated.

Remediation Air Monitoring

Remediation refers to the implementation of waste removal, treatment, and/or containment actions based on RI/FS results. Air monitoring is conducted during site remediations to ensure that cleanup activities do not pose adverse health impacts to on-site workers or downwind residents. Because the principal health concern usually involves short-term exposure, obtaining results in real time (on the order of seconds to minutes) is an important data requirement. As a rule, monitoring methods that require sample collection and subsequent off-site laboratory analysis cannot meet this requirement.

The DQO for air monitoring during site remediations is to provide real-time air contaminant data suitable for assessing on-site and off-site health impacts. Remote optical sensing can generally be used in a cost-effective manner to achieve this DQO. In a manner similar to the RI application, path-integrated concentrations measured at a known distance downwind of a remediation, together with on-site meteorology, are used to satisfy basic relationships derived from classical Gaussian dispersion theory.¹⁰ However, for this application, these data lead directly to a slightly conservative estimate of maximum plume centerline concentration at any downwind distance of concern. These maximum concentrations (in units of ppb or $\mu\text{g}/\text{m}^3$) can then be directly compared to health-based standards or action levels.

Post-Remedial Applications

Post-Remedial Air Monitoring

Periodic monitoring of a remediated source is sometimes required to ensure the long-term integrity of the treatment or containment action. Quarterly or annual ground water monitoring is most often required, but post-remedial air monitoring is sometimes a provision of the record of decision (ROD) for a site.

The DQO for post-remedial air monitoring is to ensure that contaminants do not create adverse off-site community health impacts. This DQO can be met cost-effectively using remote optical sensing in a manner identical to that described for obtaining baseline emission estimates during the RI. However, the post-remedial air monitoring program is better focused because more information is known about the site. Because the frequency with which post-remedial air monitoring is required is not likely to exceed quarterly, it is again important that it be conducted under meteorological conditions representative of reasonable worst-case emissions and transport.

The monitoring method involves the measurement of path-integrated concentrations upwind and immediately downwind of the site so that issues of source apportionment are addressed. It is important that the detection limits for the contaminants of concern are low enough so that non-detects

measured under given meteorological conditions translate to an acceptable annual risk to downwind receptors based on local climatology. Depending on local climatology, on the particular contaminant(s) of concern, on what is considered an acceptable risk, and on current instrument detection limits, this may not always be possible.

Emergency Response Applications

Emergency Response Air Monitoring

Emergency response actions are carried out for any situation that poses an imminent and substantial danger to public health and welfare. Frequently, this imminent danger is in the form of adverse health impacts arising from exposure to air contaminants by downwind populations. Air monitoring frequently represents a major need during emergency response activities.

The DQO for emergency response air monitoring is to provide real-time air contaminant data suitable for assessing off-site community health impacts. Remote optical sensing can be used to achieve this DQO in two ways. First, it can be used at a fixed downwind distance to estimate maximum plume centerline concentrations at any downwind distance of concern, in a manner identical to that described for remediation air monitoring. Second, remote sensing can provide an accurate source term estimation for input into real-time emergency response models (e.g., CAMEO) to facilitate emergency response decisions. Such models can facilitate response decisions by providing data more refined than those generated by the simple Gaussian dispersion relationships mentioned above.

LIMITATIONS

Several significant limitations exist concerning application of remote optical sensing to Superfund activities. Although the technique is very powerful and can achieve many of the necessary DQOs, its employment in the field without a comprehensive understanding of each of these limitations can jeopardize the results of the investigation. These limitations are:

1. **Contaminant Identification.** Positive identification of contaminants measured via broad-band long-path spectroscopy is accomplished by comparing the spectra of the measured contaminant to its library spectra. The "goodness of fit" between these spectra is typically established by a statistical method such as a classical least-squares analysis. As the number of interfering adsorption bands in the measured spectra increases, the certainty with which the contaminant of interest can be identified decreases. These interfering adsorption bands can arise either from other contaminants or from naturally occurring gases such as water vapor. Because of this, it is generally advisable to conduct some type of confirmatory sampling and analysis using traditional point-sampling techniques, especially when there are more than several contaminants of concern.
2. **Detection Limits.** Detection limits are derived in the field on a compound-specific basis. Several factors govern detection limits, including refraction of the beam due to thermal air currents, variations of naturally occurring interferers, and high levels at

cross-interfering target compounds. The detection limits associated with most remote optical sensing techniques are not sufficiently low to facilitate direct comparison to ambient air action levels at downwind receptor locations; therefore, this is not a recommended application. Detection limits on the order of 5 to 50 ppm-m are generally achievable for most compounds of interest.

3. **Meteorology.** Although not a limitation per se, meteorology is an important factor governing the interpretation of long-path measurement data. The most significant meteorological variable is atmospheric stability, as this controls the extent to which the plume disperses. Because containment of the plume (in the horizontal) within the beam is a requisite for Superfund application as discussed, an understanding of horizontal dispersion as a function of stability is necessary.

Understanding how stability affects plume dispersion in the vertical is especially important in the interpretation of the data. At an arbitrary distance of 50 meters downwind of a source that emits at a constant rate, the measured path-integrated concentration can vary by nearly two orders of magnitude, depending on the stability class and the associated vertical dispersion. This illustrates the need to have accurate on-site meteorological data.

4. **Area Sources.** The procedure described to derive source emission rates assumes a virtual point-source release in the absence of site-specific emissions information. The modeled downwind concentrations from large area sources will tend to be slightly higher than actual concentrations. However, the conservative nature of these calculations is generally acceptable, and often desirable, for most Superfund applications.
5. **Logistical.** Logistical concerns associated with the use of remote sensing, regardless of its application, can be significant. A clear line of sight must exist in the crosswind direction both upwind and downwind of the site. For some applications, this may involve clearing a path through existing vegetation or simply waiting for the wind to blow from some pre-determined direction.

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TABLE 1

SUPERFUND APPLICATIONS AND ASSOCIATED DQOs

<u>Superfund Application</u>	<u>DQO</u>
Site Assessment	
HRS Model scoring for the air route	To conclusively demonstrate the presence or absence of off-site migration of air contaminants.
Remedial	
RI air monitoring	To provide air contaminant data suitable for generation of accurate emission rate estimates under undisturbed conditions.
FS air monitoring	To provide air contaminant data suitable for generation of accurate emission rate estimates during pilot-scale assessments of cleanup alternatives.
Remediation air monitoring	To provide real-time air contaminant data suitable for assessing on-site and off-site health impacts.
Post-Remedial	
Post-remedial air monitoring	To ensure that air contaminants do not create adverse off-site community health impacts.
Emergency Response	
Emergency response air monitoring	To provide real-time air contaminant data suitable for assessing off-site community health impacts.

Measurements of Emissions at a Chemical Waste Water Treatment Site with an Open Path Remote Fourier Transform Interferometer

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Remote measurements of gaseous emissions from a chemical waste water treatment site were performed using quantitative Fourier transform infrared (FTIR) spectroscopic techniques. The remote open path FTIR unit was bistatic: the transmitter and the receiver were placed on opposite sides of the volume of atmosphere to be measured. The beam passed through the atmosphere in which quantitative measurements of chemical species were to be made.

Path integrated concentrations of ammonia, methanol, methylene chloride, and sulfur hexafluoride were measured with the FTIR unit along the downwind side of the waste treatment site along a horizontal beam path at various heights above ground. The concentrations as a function of height in most cases followed a monotonic curve with the greater concentrations nearer the ground as would be expected from simple dispersion models.

We used an FTIR remote sensor to measure the emissions from an equalization pond at a waste water treatment facility as part of a chemical company program to test emission models. The setup used consisted of a ir beam transmitter which was a four inch Cassegrain telescope with a glow bar ir source at its focus. The ir beam was transmitted through an atmospheric path of 60 m along the downwind shore of an equalization pond to the receiver. The receiver is a 14 inch F/6 Cassegrain telescope. The beam was recollimated with a diameter of 1.5 inches and then passed into the Michelson interferometer of the Fourier transform spectrometer. We used the simple bistatic configuration to facilitate changing the height of the beam. Measurements were made at five different heights, 1.5, 3, 5, 12, 18 ft. The different heights were obtained using two towers with five mirrors on each, as shown in Figure 1. The setup time for changing the heights was 30 to 40 minutes.

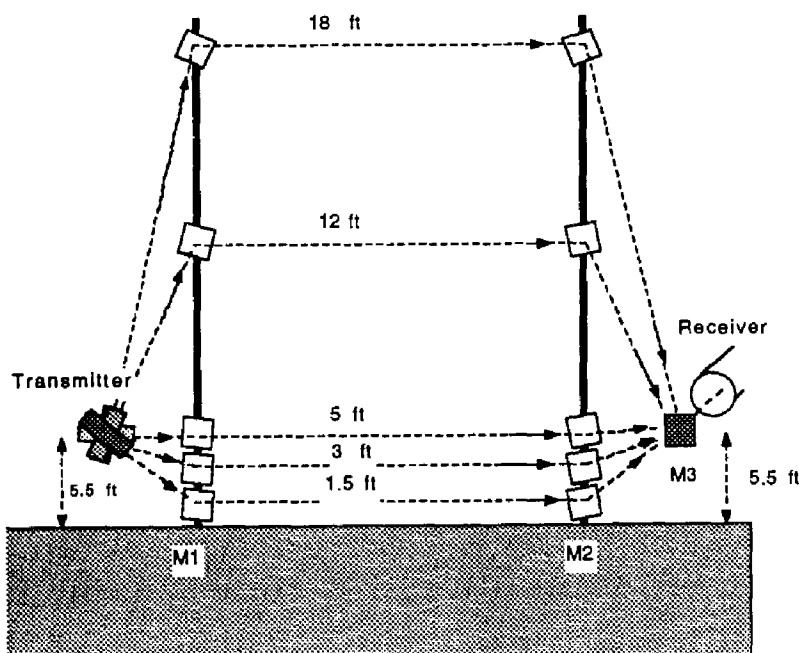


Figure 1. The Bistatic FTIR Remote Measurement Configuration Used to Vary the Elevation of the FTIR Concentration Measurements. The beam is reflected by a total of three mirrors in the field, M1, M2 and M3. For each elevation, the tilt angle of the transmitter and the mirror M3 must be adjusted.

Initially, the infrared field spectra were visually compared to clean air spectra in order to make qualitative determinations of the chemical emissions. Upon identifying the presence of methylene chloride, ammonia, methanol and sulfur hexafluoride (which was used as a tracer), we performed a classical least squares fit¹ to reference spectra of precisely known quantities of these species. These spectra are part of a library of reference spectra of 140 species, which we brought to the field stored on the computer's hard disk. Table 1 shows the results of the measurements. The concentration are averages over the 60 meter path, which is slightly larger than the width of the equalization pond (~50 m). We were able to obtain reliable measurements of sulfur hexafluoride at very low concentrations because of the extremely strong absorption feature (Q branch) which appears at 944 cm^{-1} . Two of the measurements (runs 614.07 and 615.01) were made on the side of the pond parallel to the wind direction to verify that the source of the chemicals was indeed the pond. These determinations were much lower than the downwind determinations, but since this configuration was not truly upwind, small quantities of the chemical emitted from the pond still crossed the ir beam. True upwind measurements were not attempted because they would have involved a long setup time.

We are presently investigating the sources of error in the FTIR remote sensor, in order to determine with confidence the accuracy of concentration determinations. For the present, we estimate the accuracy to be ~15 percent when the concentrations are not too close to the minimum detectable limit.

Run Number	Time	Beam Height (ft)	Effective Pathlength (m)	SF ₆		Methylene Chloride (ppb)	Methanol (ppb)	Ammonia (ppb)
				Tracer Release	SF ₆ (ppb)			
613.01	8:07	5	50	small	2.3(1.5)	0	1670(10)	500(60)
613.02	8:54	5	50	small	0	0	680(50)	58(32)
614.01	15:55	5	60	no	0	607(94)	900(40)	850(40)
614.02	17:20	3	60	no	0	1568(138)	1220(80)	910(70)
614.03	17:55	1.5	60	no	0	443(115)	1070(60)	910(70)
614.04	18:31	1.5	60	small	0	1445(156)	1270(70)	970(80)
614.05	19:07	3	60	small	0	1839(99)	1320(60)	950(50)
614.06	19:46	5	60	small	0	728(126)	1110(90)	690(70)
614.07	20:39	6.25	125	no	0	0	277(20)	176(21)
615.01	10:43	6.25	62	small	0	0	160(50)	0
615.02	13:32	1.5	62	small	0	1886(241)	1770(130)	550(110)
615.03	14:02	3	62	small	0	1123(265)	1450(150)	210(150)
615.04	14:41	5	62	small	0	1529(297)	1200(110)	320(100)
615.05	16:35	12	62	small	0	424(205)	740(100)	200(150)
615.06	17:12	18	62	small	0	0	473(30)	200(40)
615.07	17:37	18	62	no	0	612(431)	548(37)	250(40)
615.08	18:13	18	62	large*	11.3(2.6)	605(428)	540(40)	260(60)
615.09	18:38	12	62	large*	18.2(3.0)	416(156)	610(50)	270(70)
615.10	19:23	5	62	large*	18(13)	909(435)	1520(240)	190(350)
615.11	19:49	3	62	large*	25.1(1.9)	1265(105)	1570(80)	730(70)
615.12	20:12	1.5	62	large*	25.7(2.0)	1692(115)	1370(90)	840(80)
616.01	9:16	6.25	62	no	0	1300(180)	0	0

Table 1 Concentration Values for all Field measurements at the Equalization Pond. The first three numbers in the file names are coded for the dates June 13, 14, 15 and 16, 1989, and the suffix is the measurement sequence number. The "effective" pathlengths are the portions of the total pathlengths where the chemicals were present. The "small" SF₆ tracer release are a factor of 10 smaller than the "large" releases. The small releases resulted in concentrations at the beam position which were lower than the minimum detectable limit. The numbers in the parentheses are the estimated standard deviation of the least squares fit propagated to the concentrations determinations. The italicized rows (runs 614.07 and 615.01) were measured in an "upwind" configuration.

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APPLICATION OF A HENE LASER TO HYDROCARBON LEAK DETECTION OVER AN OIL FIELD

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As a part of an oil field modernization study, a laser-based hydrocarbon leak detection system was evaluated on the H. O. Mahoney lease in Yoakum County, Texas. The purpose of the test was to determine if small amounts of methane gas associated with oil leaks could be reliably detected in the atmosphere by long-path laser measurements.

The test system consisted of a 6 mW HeNe laser tuned to emit radiation at 3.392 μm , a mechanical chopper, a lead sulfide detector, a lock-in amplifier, and a 15 cm diameter simultaneous transmitter/receiver telescope. The signal was returned to the detector with a 6 cm cube retroreflector of 30 arc second accuracy. The response of the laser return signal to both ambient concentrations of methane and to controlled releases of methane gas was measured over a range of wind speeds and air temperatures.

The cross-plume concentration of methane was determined with the HeNe laser and this value was compared to predictions from a 2-D plume dispersion model. In general, agreement between observations and model predictions was excellent, even though the predictability of the model is uncertain at downwind distances less than 100 m. Poor agreement between the observed methane column density and the model result usually occurred during light and variable winds. These observations also showed that the signal-to-noise ratio of the single-beam system is strongly dependent on temporal fluctuations in the atmospheric concentration of methane and on local meteorological conditions (e.g., strong solar insolation, dust, etc.)

INTRODUCTION

In 1987, Mobil Oil Inc. modernized an oil field production facility in the Wasson field of west Texas. A part of that program involved the testing of a remote detection system that would provide early warning of leaking petroleum from storage tanks, flow lines, process equipment, and pumps on the lease. The chief concern was the environmental detection of leaking oil, but because oil is not readily detected by remote methods, methane gas, which is a major component of the produced fluids, was selected as the tracer of interest.

After examining several optical systems, we selected a continuous wave HeNe laser tuned to $3.392\mu\text{m}$. This laser is an ideal choice for the detection of atmospheric methane because its emission wavelength is nearly coincident with one of the rotational-vibrational absorption bands of methane (Kucеровsky et al., 1973; Murray, 1978; Patel, 1978; Grant and Menzies, 1983). Previous studies by Kucеровsky et al., (1973); Grant, (1986) have clearly demonstrated the utility of this technique to long path-length monitoring of atmospheric CH_4 .

In this report we describe the response characteristics of a double-ended, single beam, HeNe laser to point-source releases of methane gas on the H. O. Mahoney lease. The purpose of the test was to determine: (i) fluctuations in the ambient concentration of methane on the lease and (ii) response characteristics of the HeNe laser to small, controlled, upwind releases of methane gas.

EXPERIMENTAL

Instrumentation

The test breadboard unit consisted of a 6 mW HeNe laser (Spectra-physics Model 127) tuned to $3.392\mu\text{m}$, a mechanical chopper for beam modulation, a cooled, lead sulfide detector, a lock-in amplifier for signal processing, a 15 cm simultaneous transmitter/receiver telescope, and a strip-chart recorder (Figure 1). Both transmitting and receiving signals were propagated along the same optical axis by the use of a double-sided secondary mirror in the Newtonian transmitter/receiver telescope. Operational parameters for the laser system are shown in Table 1.

Physical Setting

The H. O. Mahoney lease is located in the Wasson field of Yoakum County, Texas (Fig 2). The lease contains 16 producing wells (40 acre spacing) and nine CO_2 injector wells, with a centrally located tank battery that consists of storage tanks and process equipment (Fig. 2). Flow lines on or near the surface of the ground transport oil and gas from the wells to the tank battery, thus likely sources of leaking oil and methane gas will be at or near ground level. The H. O. Mahoney lease is particularly well-suited for the long-path length monitoring of methane gas because the topography is relatively flat and only partially covered with low-growing plants to approximately 3 ft. The only significant obstacles to the laser beam are the storage tanks near the center of the lease; they are approximately 20 ft high.

The ambient concentration of methane (includes other absorbing species at $3.392\mu\text{m}$) was determined along three transects located near the center of the lease (Fig. 2). These transects were chosen to provide ambient atmospheric conditions under varying wind trajectories.

Point releases of methane gas were also made along the same three transects, depending on the local wind conditions and specific objectives. Methane gas (98% pure) from a standard 220 ft³ cylinder was released at rates of 330 mg CH₄/s and 660 mg CH₄/s (1500 ft³/d and 3000 ft³/d, respectively) approximately 1 m above the ground. Flow rates of methane gas were determined with a flow meter attached to the tank and a two-stage pressure regulator. Wind velocities were determined with a hand-held, digital anemometer; average and range of velocities were determined over a one minute time period at the beginning and near the end of the release period. Experimental conditions are displayed in Table 2.

RESULTS AND DISCUSSION

Ambient Conditions

Figure 3 shows a 15 min record of the laser response to the ambient atmosphere upwind of the tank battery. In order to compress the analog record, two second intervals of the power ratio (P_r/P_t) were averaged for 12 seconds and the resulting mean value plotted. This ratio is the received power (P_r) relative to the transmitted power (P_t) as determined on a strip-chart recorder. Peak-to-peak fluctuations for low wind conditions upwind of the tank battery (Fig. 3a) were only 4%, a value typically recorded during the early evening and early morning hours. Not shown in this particular record are the relatively infrequent, but large amplitude, low frequency fluctuations that occurred during light and variable winds.

During periods of high solar insolation, peak-to-peak fluctuations in the power ratio generally increased (Fig. 3b). In this particular record the peak-to-peak fluctuation was 5%, but variations up to 10% were noted during some afternoon tests. Fluctuations of this size are assumed to be related to density fluctuations in the lower atmosphere brought about by strong ground heating, but thermally induced electrical effects in the laser and associated signal processing equipment may also have been important. The afternoon shade temperature reached 106°F on May 23 and May 24.

Figure 4 shows the relative power response of the HeNe laser to small releases of methane gas over a 90 min period. In this case the analog signal was averaged for 1 min. Observed reductions in the received signal varied from 10-20% for the small releases (330 mg CH₄/s) to 20-40% for the larger releases (660 mg CH₄/s). Rapid fluctuations in the signal were evident as the methane plume wandered in and out of the laser beam. In some cases the laser response did not return to baseline (approx. 90%) after the gas had been turned off. It is likely that insufficient time was allowed for the methane plume to reach stationary conditions.

Plume Dispersion Model

In order to estimate the response of the laser return signal to a leak of methane gas anywhere on the lease (maximum range approximately 1 km), methane releases at relatively short distances were modeled with a stationary, 2-D, plume dispersion model (e.g., Csanady, 1973). Because the HeNe laser measures the column density of methane in the atmosphere, an integrated form of the plume dispersion model was adopted. Mean wind speeds were estimated from our measurements, while estimates of the dispersion coefficient in the z-direction (e.g., σ_z) were linearly extrapolated from Gifford's (1961) values. Assuming that the plume trajectory was orthogonal to the laser beam and, at the same elevation as the laser beam, the solution to the plume dispersion model is:

$$C_m = \frac{Q[1 + \exp\{-2h^2/\sigma_z^2\}]}{\sqrt{2\pi}u\sigma_z}$$

where Q is the release rate (mg CH_4/s), C_m is the column density of methane (mg CH_4/m^2), u is the mean wind speed (m/s), and h is the elevation of the laser beam (in this case, 1 m).

Similarly, the laser response to a methane plume can be estimated from the background-corrected LIDAR equation (Grant, 1986; eqn. 1). The result is:

$$C_1 = - \frac{\ln(P_1/P_b)}{2\alpha}$$

where C_1 is the predicted column density of methane, P_1 is power response of the laser in the methane cloud, P_b is the power response to the ambient methane concentration, and α is the methane absorption coefficient. The methane absorption coefficient is $770 \text{ m}^{-1} \text{ atm}^{-1}$ (Grant, 1986).

Methane concentration, as determined by the HeNe laser (C_1) is compared to the calculated value (C_m) in Table 3. Atmospheric stabilities (i.e., A-D) were estimated from the wind velocity, solar insolation, and cloud cover at the time of the observations. There is excellent agreement between the laser response and the prediction of the plume dispersion model for most of the experimental runs. The average difference between the observed and predicted values is approximately 30%, which is remarkably good agreement when one considers the uncertainties in the model predictions at short downwind distances so near the ground.

Significant departures between the observed and expected results were noted in experiments 6, 10, and 11. In experimental runs 6 and 10, the methane column density, as determined by the laser, was lower than the model prediction. There are several possible reasons for this including, misalignment of the methane plume and the laser beam, mean wind speed estimate was too low, or the model value for the vertical dispersion coefficient was too low. In run 6 winds averaged less than 1 m/s, thus there is good reason to believe that the laser beam only occasionally intersected the methane plume.

The difference between observed and model methane concentrations in Run 11 was unique in that the laser response was larger. In this case our estimate of the atmospheric stability may have been in error. By assuming a more stable atmosphere (C or D), the model cross-plume methane concentration would have been larger and consequently in better agreement with the observed value.

CONCLUSIONS

The single HeNe laser has been shown to be a reliable remote sensing instrument for the detection of methane gas in the atmosphere. Its usefulness as a methane leak detector, however, is limited by ambient fluctuations in the background atmospheric concentration of methane and local meteorological conditions. It is anticipated that the signal-to-noise ratio of the HeNe laser system could have been improved significantly by employing two laser wavelength differential measurement to minimize fluctuations in the ratioed laser return signals due to water vapor, atmospheric aerosols, and atmospheric turbulence.

Good agreement between the cross-plume optical density of methane and the 2-D plume dispersion model in this study suggests that the vertical dispersion coefficient of Gifford can be linearly extrapolated to downwind distance less than 100 m. Alternatively, the HeNe laser may be used to measure vertical dispersion scales in the atmosphere using methane as a tracer.

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Table 1. Component parameters for the HeNe laser system.

COMPONENT	PARAMETER
HENE Laser	Spectra-Physics 127
Power	6mW @ 3.392 μ m
Divergence	0.66 mrad
Beam Width	1.25 mm
Chopper	
Frequency	110 Hz
Receiver Telescope	Newtonian
Diameter	22.86 cm
Focal Length	76 cm
Detector	PbS
Diameter	2 mm
D*	1.3×10^{10} mm Hz ^{1/2} W ⁻¹
Retroreflector	6.35 cm (dia.)
Coating	Au with MgF ₂ overcoat

Table 2. Summary of controlled release experiments performed on the H. O. Mahoney lease, Wasson field, Texas. Q is the methane release rate, X is the perpendicular distance between the release point and the laser beam, and R is the distance to the retroreflector. The location of the transects is given in Figure 1.

Exp. No.	Transect	Date/Time	Q mg CH ₄ /s	X m	R m
1	A	May 23, 1989/1540 hrs	330	67	100
2	A	"	660	67	100
3	A	May 24, 1989/1600 hrs	330	41	200
4	A	"	330	73	200
5	A	"	660	73	200
6	B	May 23, 1989/2000 hrs	330	55	100
7	B	"	330	55	100
8	C	May 23, 1989/1300 hrs	330	36	100
9	C	"	330	36	100
10	C	"	660	36	100
11	C	May 9, 1989/1700 hrs	330	61	100
12	C	May 9, 1989/1600 hrs	330	20	100
15	C	May 9, 1989/1630 hrs	330	36	100

Table 3. A comparison of observed (C_l) and predicted (C_m) methane column densities for 11 experimental runs. Atmospheric stabilities according to Gifford (1961) are shown in parentheses. Stability class A is the most unstable; D the most stable.

RUN No.	Q mg CH ₄ /s	X m	U m/s	C_l mg CH ₄ /m ²	C_m mg CH ₄ /m ²
1	330	67	2.5	25	26 (B)
2	660	67	2.5	49	52 (B)
3	330	41	3.0	48	35 (B)
4	330	73	3.0	23	20 (B)
5	660	73	3.0	70	61 (C)
6	330	55	0.5	92	156 (B)
8	330	36	2.0	34	36 (A)
10	660	36	2.0	40	72 (A)
11	330	61	4.0	32	18 (B)
12	330	18	6.0	55	48 (D)
15	330	36	4.0	39	51 (C)

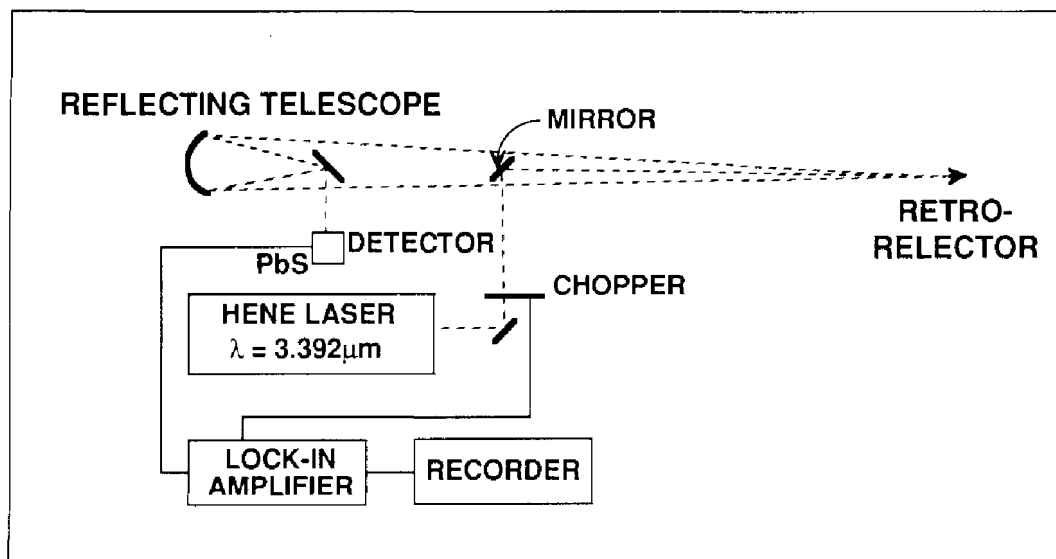


Figure 1. Schematic diagram of HENE breadboard unit. Operational parameters for the laser, the Newtonian telescope, and the detector are listed in Table 1.

H.O. Mahoney
Lease
Yoakum Co.
Texas

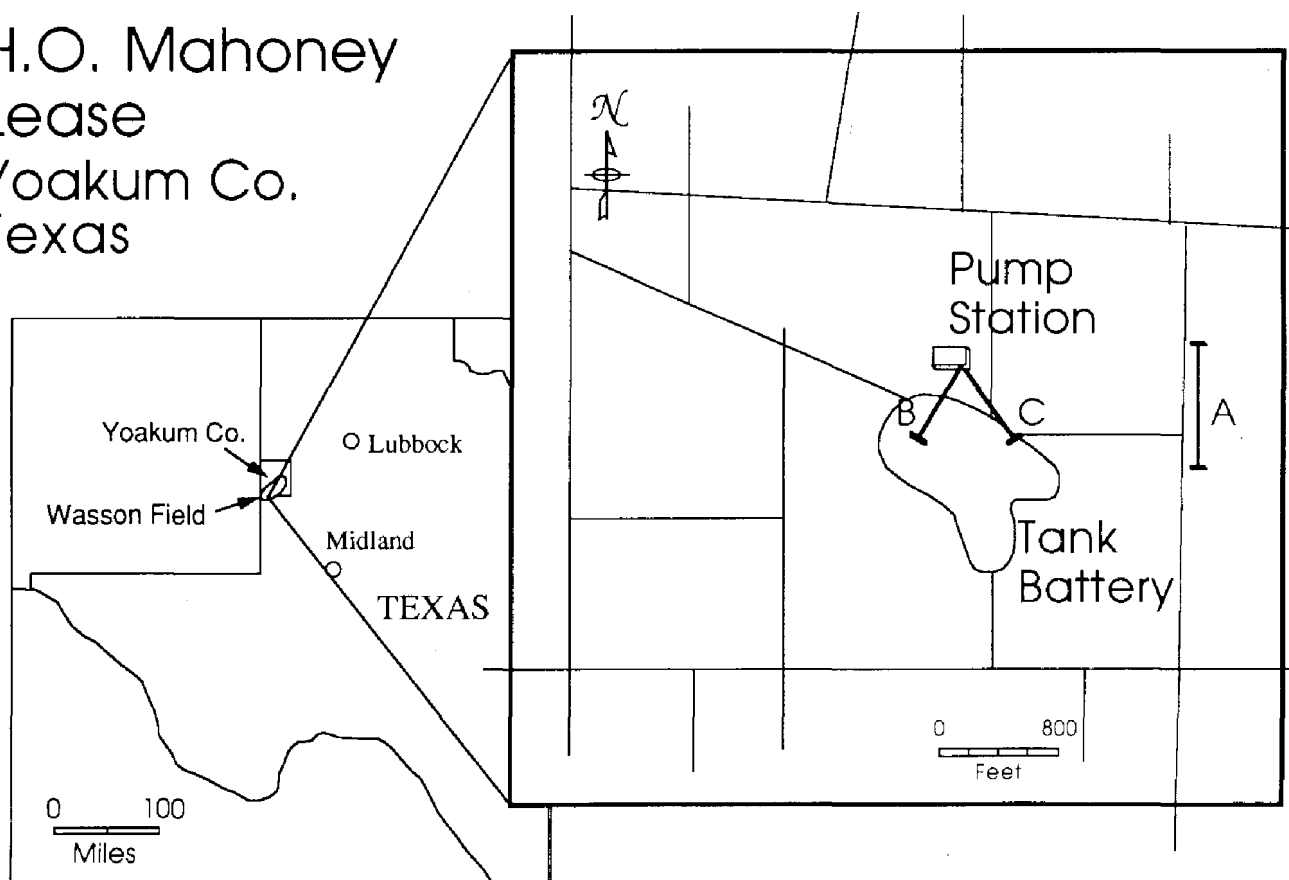
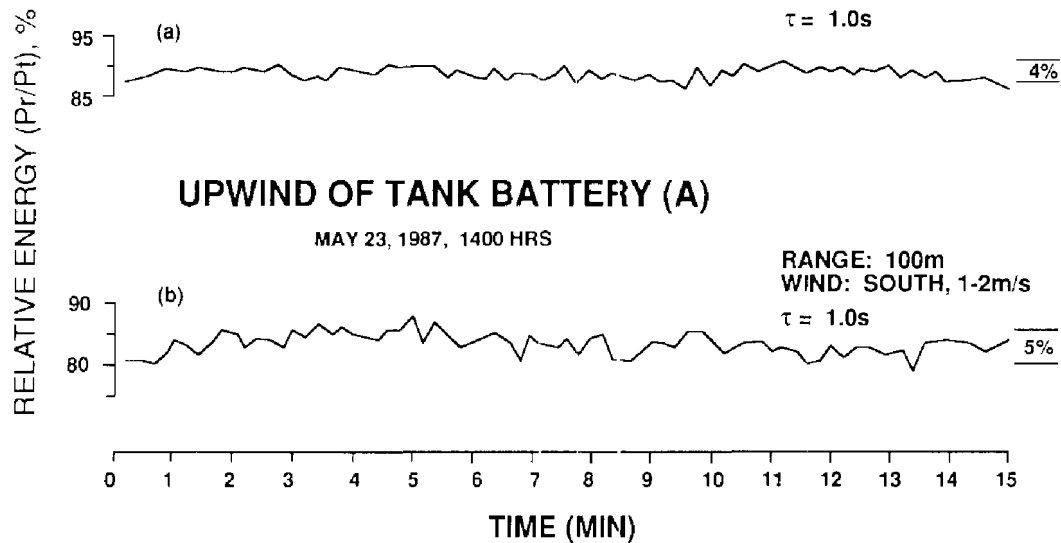


Figure 2. Location of the H. O. Mahoney lease in west Texas. Measurements were conducted along transects A, B, and C (see Table 2).

UPWIND OF TANK BATTERY (B)

MAY 23, 1987, 2000 HRS

RANGE: 100m
WIND: WEST, 0-0.5m/s
 $\tau = 1.0s$



UPWIND OF TANK BATTERY (A)

MAY 23, 1987, 1400 HRS

RANGE: 100m
WIND: SOUTH, 1-2m/s
 $\tau = 1.0s$

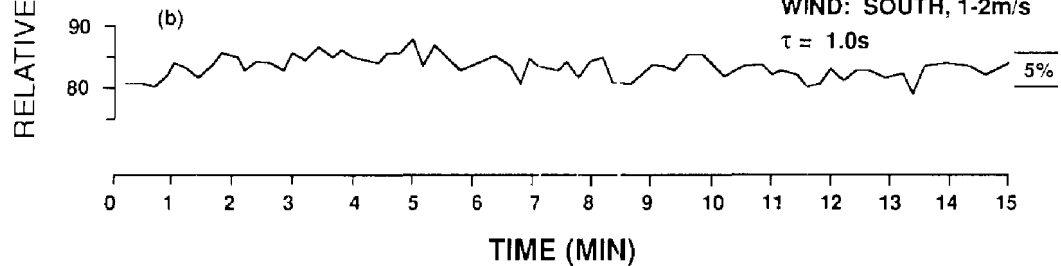


Figure 3. Relative response of the HENE laser to ambient conditions along transects A and B. Peak-to-peak fluctuations in the signal were 4% and 5% respectively, for 12 s averages.

UPWIND OF TANK BATTERY (B)

RANGE: 100m (330 ft)
DISTANCE (X): 55m (180 ft)
WIND: VARIABLE, <1m/s (<2mph)
DATE/TIME: 5/23/89, 2000 Hrs

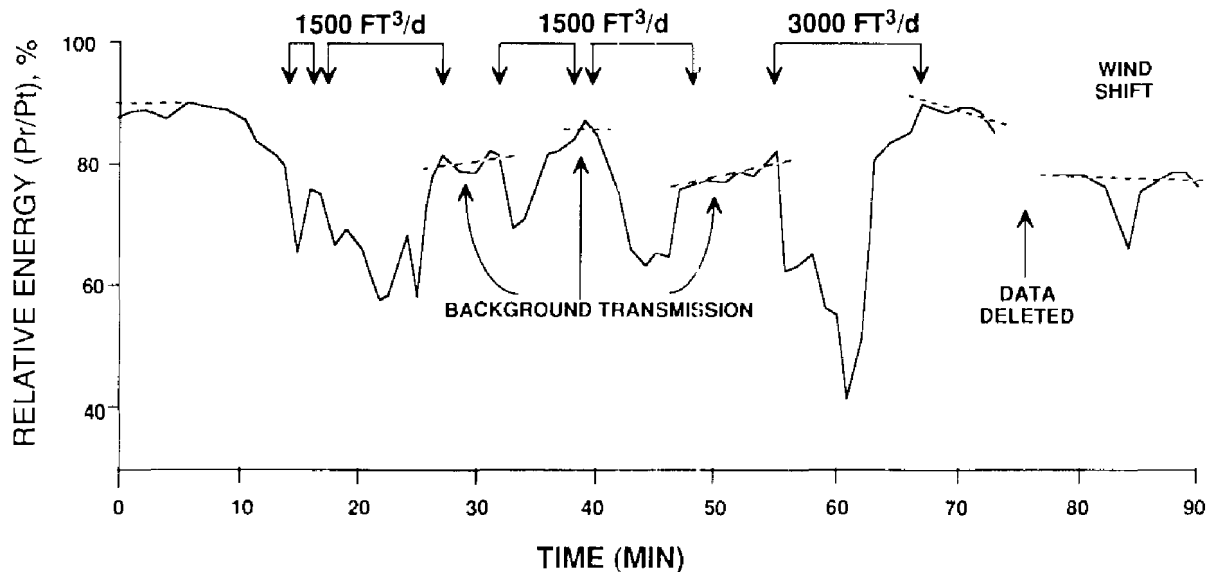


Figure 4. Relative response of the HENE laser to point releases of methane gas along transect B. The amounts of gas released were 330 mg CH₄/s (1500 ft³/d) and 660 mg CH₄/s (3000 ft³/d).

EVALUATION OF COMMUNITY EXPOSURE TO AIRBORNE SARA
TITLE III SECTION 313 CHEMICALS EMITTED FROM
PETROLEUM REFINERIES

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Radian Corporation conducted an ambient air monitoring study for the American Petroleum Institute (API) to estimate the impact of petroleum refinery emissions on air quality at the fenceline. Three refineries were monitored over three consecutive days in the spring and early summer of 1988. The target list of chemicals included twenty five (25) SARA Title III Section 313 air toxics in several classes: hydrocarbons, chlorinated hydrocarbons, acid vapors, ammonia and metals.

Eight sampling sites were located around each refinery to monitor the air both upwind and downwind of the emission sources. Meteorological measurements were made during the three days of sampling. Sampling methods were based on a combination of filters, sorbents and evacuated metal canisters. Analytical detection limits in the range 0.2 - 20 micrograms per cubic meter ($\mu\text{g}/\text{m}^3$) were achieved for the target chemicals.

The elements of the study design will be presented. The methods for sampling, analysis and data treatment will be reviewed and an overview of the air monitoring results will be presented. An evaluation of the monitoring methods will be given, as well as conclusions regarding the potential for community exposure.

Experimental Methods

The target list of airborne chemicals to be measured consisted primarily of twenty five (25) species reported by one or more of the refineries under SARA Title III Section 313. The target species would be present in ambient air in the form of a gas, vapor or particulate matter. No single sampling and analytical method was feasible so the target chemicals were grouped according to their monitoring methodology. Table I lists the target chemicals in four groups of primary target chemicals (groups 1, 4, 6 and 7) and one group (group 9) of secondary target chemicals.

The four primary target chemical groups contain 25 SARA Title III Section 313 compounds. Group 9 contains 14 SARA chemicals and 11 non-SARA indicator compounds and was monitored at only one third the frequency of groups 1, 4, 6 and 7.

The sampling and analytical approach for each target chemical group is shown in Table II. The target limits of detection (LOD) apply to 24-hour integrated air samples. Air sample volumes over 24-hours were nominally 144 liter for all groups, except 1440 liter for the group 7 metals and 15 liters for the group 9 canister samples.

Eight sampling sites were arranged around each refinery according to the strategy shown in Figure 1. This strategy was designed to measure ambient air concentrations at fixed distances in the range 1000-5000 feet from the refinery center. Multiple sampling sites would help assure upwind and downwind coverage even if the wind direction were variable over 24-hours. Radian operated a portable meteorological station throughout the three days of air sampling.

Field quality control consisted of a field duplicate set (sites 3 and 4) and a field blank (site 10) for each 24-hour sampling period. In addition, filter and sorbent media were spiked with selected target chemicals from groups 1, 3, 6, and 7. These spiked media were air sampled and analyzed for recovery to help validate the sampling approach.

Air Monitoring Results

The ten target chemicals detected with the highest frequency around each refinery are listed in Table III along with their measured concentration range in $\mu\text{g}/\text{m}^3$. Aliphatic hydrocarbons detected in these ambient air samples were summed into carbon number groups: C4 to C5, C6 to C8, and C8+.

Other than these aliphatic hydrocarbons, benzene, toluene and xylene were the major target hydrocarbons found in this study, and sulfuric acid was the only non-hydrocarbon found at all three refineries. Figure 2 summarizes the air concentration data for benzene, toluene, m,p-xylene and ethylbenzene for the three days of monitoring at each of the three refineries. The daily mean and maximum air concentrations over all 8 sampling sites is shown.

Conclusions

The sampling and analytical approach was demonstrated to be a cost effective way to measure ambient air concentrations for several classes of air toxic chemicals in a short term, intensive monitoring campaign.

Benzene, toluene, and xylene were the target hydrocarbons seen with the highest frequency around the three refineries studied, but they were generally present at low concentrations, eg <1 to 23 $\mu\text{g}/\text{m}^3$ for benzene.

TABLE I. THE API REFINERY STUDY: LIST OF PRIMARY AND
SECONDARY TARGET CHEMICALS

PRIMARY TARGET CHEMICALS

Group 1

Anthracene	Ethyl Benzene	Toluene
Benzene	Methyl t-Butyl Ether	1,2,4-Trimethylbenzene
1,3-Butadiene	Methyl Ethyl Ketone	m-Xylene
Cumene	Naphthalene	o-Xylene
Cyclohexane		p-Xylene

Group 4

Carbon Disulfide	Ethylene Dibromide	Ethylene Dichloride
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Group 6

Ammonia	Hydrogen Fluoride	Sulfuric Acid
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Group 7

Cadmium	Chromium	Nickel	Selenium	Vanadium
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SECONDARY TARGET CHEMICALS

Group 9

Benzene	Additional non-SARA
1,3-Butadiene	Indicator Compounds:
Cumene	t-Butyl Benzene
Cyclohexane	n-Hexane
Ethylene Dibromide	n-Heptane
Ethylene Dichloride	Isohexane
Ethyl Benzene	Isooctane
Ethylene	Methylcyclohexane
Methyl t-Butyl Ether	3-Methylhexane
Methyl Ethyl Ketone	3-Methylpentane
Toluene	n-Pentane
1,2,4-Trimethylbenzene	Trichloroethylene
m,p-Xylene	Tetrachloroethylene
o-Xylene	

TABLE II.

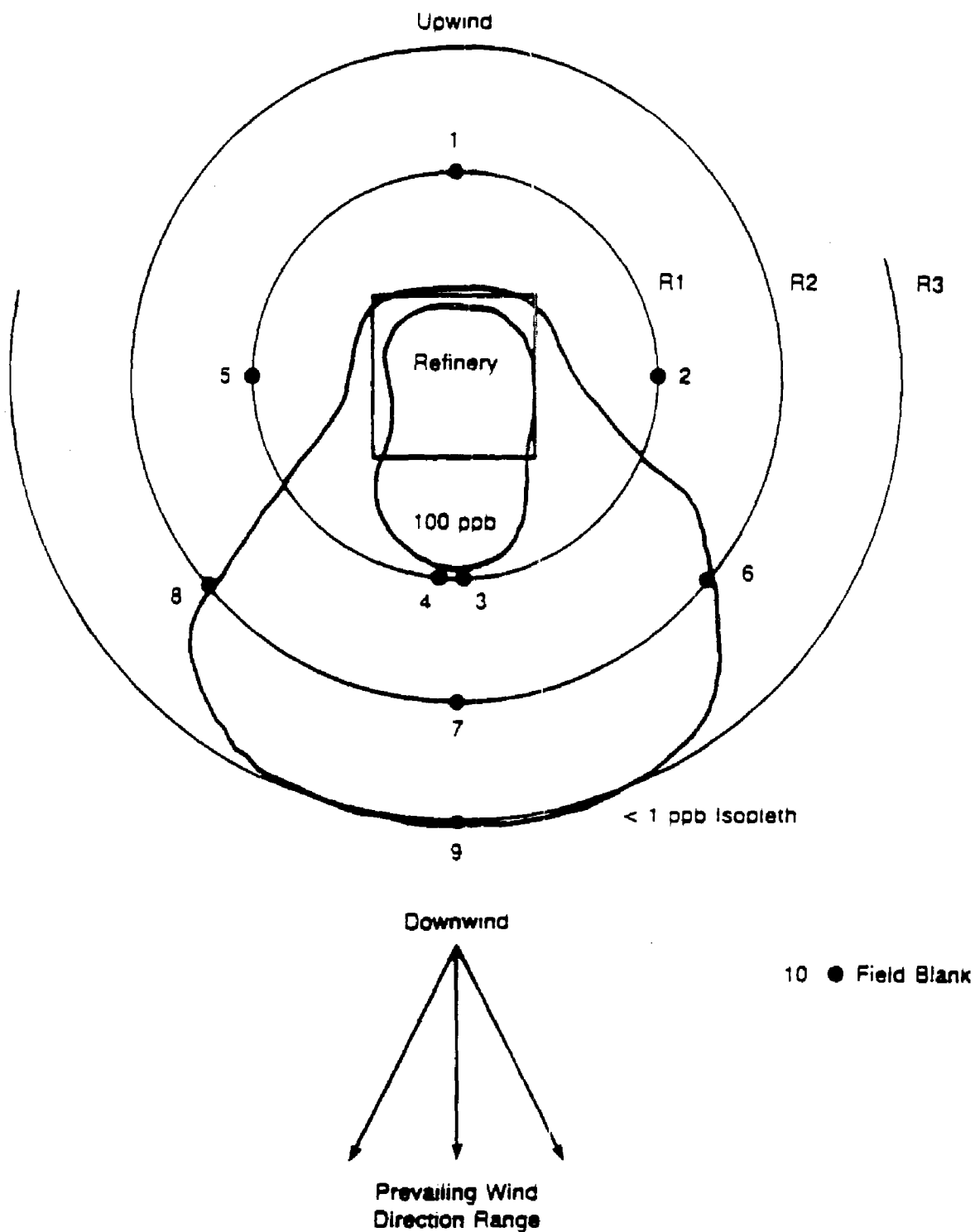
SAMPLING AND ANALYTICAL TECHNICAL APPROACH

Group #	Chemicals in Group	Method Source	Sampling Medium	Analytical Method	Target LOD (ppbv)
1	Hydrocarbons and C-H-O	NIOSH	Filter + Charcoal tube	GC-FID	2-20
4	Electrophilic Compounds	NIOSH	Charcoal tube	GC-ECD	1-5
6	Acids	NIOSH	Silica gel tube	IC	5-20
	Ammonia	NIOSH	Silica gel tube	Color	2-10
7	Metals	NIOSH	Filter	ICAP	0.5-5
9	Hydrocarbons, C-H-O, C-H-Cl	Radian	Canister	HRGC-MD ^a	0.5-1

^aMD = multiple detection = FID + PID + HSD.

TABLE III. THE TEN CHEMICALS DETECTED WITH THE HIGHEST FREQUENCY IN THE
AMBIENT AIR AROUND EACH REFINERY

Refinery	Chemical Name	Percent Frequency Detected	Concentration Range (ug/m ³)
1	C4 - C5 Hydrocarbons	89	1 - 120
	Ammonia	67	<4 - 9.9
	C8+ Hydrocarbons	56	1 - 23
	Sulfuric acid	44	<30 - 56
	C6 - C8 Hydrocarbons	44	2 - 39
	Ethylene dichloride	33	<1 - 44
	Toluene	22	<1 - 3
	m,p-Xylene	11	<1 - 4
	Benzene	11	<2 - 3
	Chromium	7	<0.3 - 0.5
2	Toluene	96	<1 - 42
	C4 - C5 Hydrocarbons	96	7.7 - 130
	C6 - C8 Hydrocarbons	93	1 - 350
	Benzene	89	<1 - 19
	m,p-Xylene	81	<1 - 33
	Sulfuric acid	41	<20 - 130
	o-Xylene	30	<1 - 11
	C8+ Hydrocarbons	26	2 - 84
	1,2,4-Trimethylbenzene	22	<1 - 6.4
3	Ethylbenzene	19	<1 - 9.0
	Toluene	100	2 - 23
	C4 - C5 Hydrocarbons	100	5 - 190
	C6 - C8 Hydrocarbons	100	8.6 - 470
	Benzene	70	<1 - 23
	C8+ Hydrocarbons	63	1 - 40
	Sulfuric acid	63	<20 - 640
	1,2,4-Trimethylbenzene	52	<1 - 4
	Ethylbenzene	48	<1 - 5
	m,p-Xylene	24	<1 - 19
	o-Xylene	14	<1 - 6.9

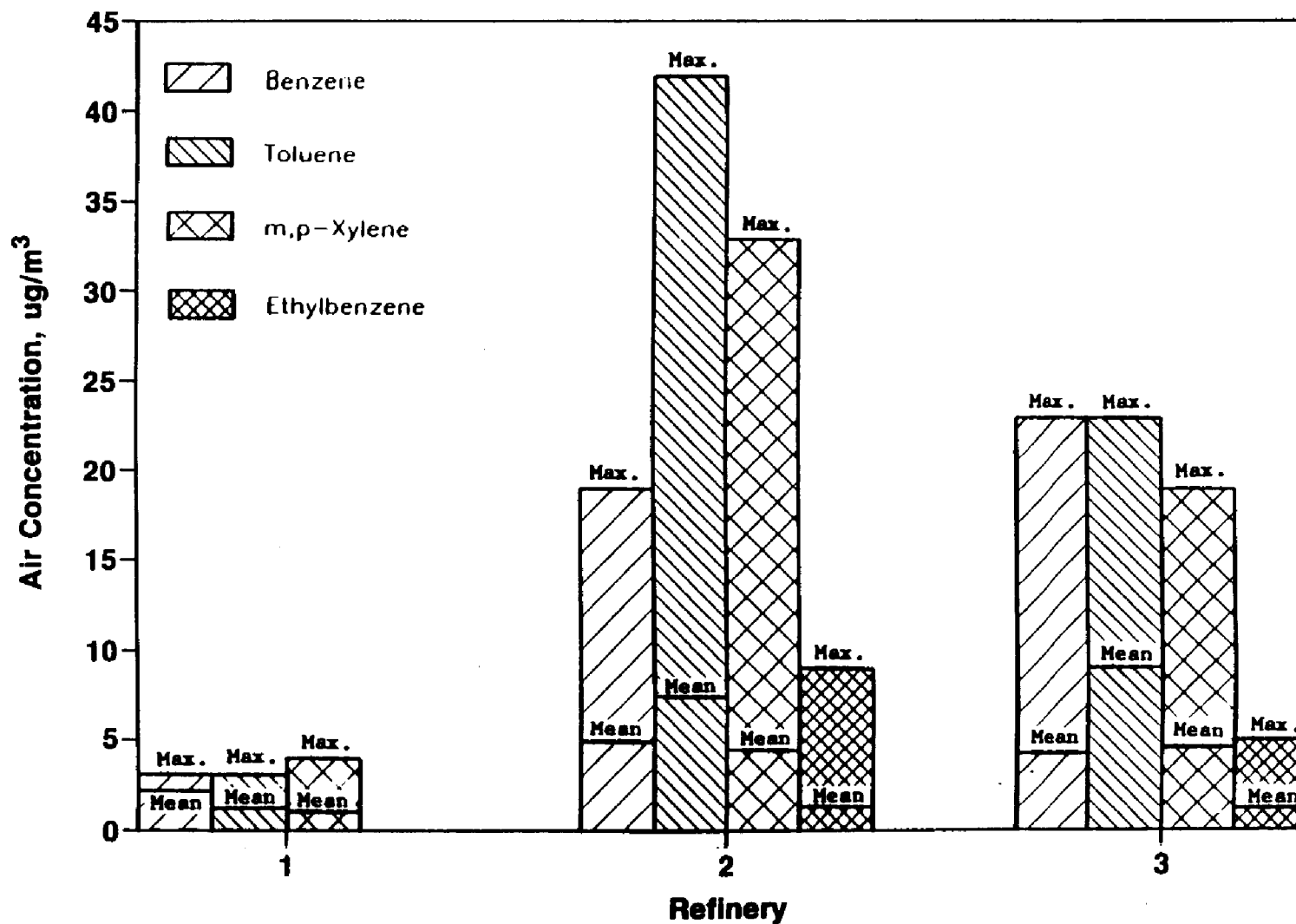


**Diagram of the Proposed Placement of
Ten Sampling Sites Around the Refinery**

FIGURE 1.

FIGURE 2.

Hydrocarbons Detected At High Frequency Daily Maximum Concentration And Mean For Three Days



DEVELOPMENT OF A TECHNICAL APPROACH FOR DETERMINING THE
VOLATILIZATION RATE OF HYDROCARBONS FROM A LANDFILL USING BOTH
MODELING AND DIRECT EMISSION MEASUREMENT TECHNIQUES

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A technical approach was developed to determine the fugitive total non-methane hydrocarbon emissions during landfilling operations. The landfill accepts soils contaminated with hydrocarbon petroleum products.

The landfilling operation was simulated by a series of waste handling operations that approximated the operation. This was necessary in order to develop a technical approach that could generate representative emission rates from the operation. The operation included a 24-to-30 hour cycle during which soils were delivered, unloaded, stock-piled, spread over the working face of the landfill, and compacted. The challenge of the program was to develop a testing and modeling strategy that could generate emission data to represent this event.

The technical approach developed to collect these emission data included a modeling exercise using the CHEMDAT6 models and field testing using the EPA Surface Isolation Emission Flux Chamber Technology. The testing strategy included direct emissions measurement of eight different loads of contaminated soil conducted over the active operation cycle of the landfill. These time-weighted emissions data were then used to estimate the total non-methane hydrocarbon emissions from the landfill.

Introduction

ENVIRON Corporation was contracted by a California landfill site owner to prepare an Authority to Construct application. The landfill is a Class I hazardous waste landfill located at an existing treatment, storage, and disposal facility (TSDF). In order to prepare the required non-methane hydrocarbon (NMHC) emission estimates, ENVIRON used the RTI land treatment model included in the EPA's CHEMDAT6 series of models.

In addition to the estimate of NMHC or reactive organic compounds (ROC) emissions obtained by using descriptive information from the landfill operation, total petroleum hydrocarbon concentration data, and modeling, ENVIRON contracted Radian Corporation to measure ROC emission rates. A protocol was developed and employed to obtain ROC emission rates using the EPA recommended emission isolation flux chamber.

Technical Approach

The basic approach used to study the emissions event was to model emission rates using available emission models and waste characterization data and to measure emission rates from representative landfill waste. Both approaches for obtaining emission rates have advantages and limitations. The advantage of the modeling is that an emission rate estimate can be obtained by imputing representative data into a specific model using limited measurement data and resources. The disadvantage of modeling is that the input data may not represent the volatile potential of the waste material. In addition, models provide estimates of dominant emission process and are not expected to accurately represent all facets of the emissions event, site conditions, and variables that have an affect on the emissions event. As such, emission estimates derived by modeling may be limited by discrepancies between the idealized system considered in the model and actual site characteristics.

Direct emissions measurements provide the most accurate and representative emission rate estimates with measurable precision. However, as with all measurement approaches, data must be collected that are representative of the emissions event. This may require testing in many locations following a labor intensive sampling schedule. Most testing is specific to a waste material, site conditions, and often times environmental conditions. Thus, measurements may be representative of a particular waste and specific site conditions, but data from this particular test may not be useful in understanding the emission event or the time-dependent emission rate.

For this testing and modeling effort, the objective was to use model input data and to conduct testing in order to represent maximum daily ROC emissions. Model inputs were selected to represent the typical material disposed of at the landfill. In addition, other model input parameters were used, including soil moisture and porosity that approximated average site conditions. The field test included screening waste loads and selecting materials for testing. Waste selected for

measurement included: gasoline contaminated soils (5 tests); diesel contaminated soils (1 test); refinery waste soils (1 test); and crude oil contaminated soils (1 test). The incoming loads of waste were screened by reviewing the waste manifest. The mix of waste types selected for testing conservatively represented the types of materials disposed of at the landfill.

The measurement event simulated the landfilling operation by placing the waste in the landfill and spreading it as is done under normal operation. Testing was conducted over a 24-hour (or longer) period. Waste samples collected from the selected loads were analyzed for total petroleum hydrocarbon (TPH), porosity, and moisture content.

Direct Measurement

The sampling procedure employed was the surface isolation emission flux chamber technique¹. Real-time VOC emission screening was performed during each isolation flux chamber measurement using a Foxboro Corporation Organic Vapor Analyzer (OVA) Model 108 calibrated with methane-in-air gas standards. Following placement of the flux chamber, the OVA was attached to the sampling line of the chamber. After steady-state conditions were realized in the chamber, samples were collected by syringe and analyzed by the on-site gas chromatograph. In addition, samples were collected in stainless steel canisters and analyzed off-site by gas chromatography. The results were reported as total non-methane hydrocarbon [parts per million by volume of carbon (ppmv-C)].

Results

The collection of physical and chemical waste characteristic data coinciding with the flux chamber measurements provides a small but informative data base which can be used to compare emission rates estimated by the RTI land treatment model contained in CHEMDAT6 to flux chamber measurements. Of the eight loads tested, five provided meaningful comparisons. Some or all of the input data required for the model were unavailable for the remaining loads.

Using the CHEMDAT6 model with load-specific chemical and physical data, the time sequence of NMHC flux was estimated for each of the loads for which appropriate input data were available. Figure 1 provides sample CHEMDAT6 model input and output. Figure 2 illustrates the measured emission rates for a load of soil contaminated with gasoline at various times following initial exposure of the waste, as well as emission rates estimated by the model where appropriate. From the eight tests, it was seen that agreement between the model and measurements was good in some cases, but very poor in others. It may be that, in cases of poor agreement, most of the volatile constituents had volatilized before the measurements began. If that occurred, the characterization of the remaining hydrocarbons as gasoline would have produced significant overestimation of the emission rates, relative to measured values.

Figure 3 is a scatter plot of measured vs. estimated NMHC emissions for the ten hours following placement of waste in the landfill. Data for five of the eight loads are plotted. The diagonal line has a slope of one, representing agreement between the methods. Load 2 (diesel-contaminated soil) was the only load for which the measured emissions over the first 10 hours exceeded emission estimates using the model. For the remaining loads, measured emissions appeared to be well correlated to estimated emissions, but significantly lower.

The average measured total emissions from the testing of materials over the first ten hours was 2.1×10^{-3} g/cm². This value is considerably lower than the emissions estimated *a priori* for the period of daily operations of the proposed landfill using the model. The average emission rate for the modeled test cases was 6.1×10^{-3} g/cm².

Conclusions

This study is unique in that two very different emissions estimation approaches were used to estimate emission rate data representing ROC emissions from the same source, an active landfill. Both approaches were used properly and generated emission estimates that, in some cases, compared well with each other. Either approach used properly and independent of the other would have provided an acceptable estimate of the ROC emission rate.

The following conclusions are offered:

- 1) The CHEMDAT6, RTI land treatment model has application for estimating air emissions from hazardous waste landfills, but may over estimate emissions substantially.
- 2) Emission rate data can be obtained using modeling equations, provided that the model represents the dominant emissions event and input data are realistic.
- 3) The EPA recommended emissions isolation flux chamber has application for measuring emissions from landfills.
- 4) Direct emission measurement approaches provide acceptable data so long as the techniques are properly executed and the testing strategy represents the emissions event.
- 5) Average emissions data from measurements over appropriate time periods and for representative waste can be used to describe emissions over larger cycles (yearly emissions) and for a variety of waste materials.
- 6) Indicator parameters, like TPH in solids, may not provide an accurate representation of volatile characteristics of waste materials.

References

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```

LAND TREATMENT MODEL DATA
(open landfill, waste pile)
L>Loading (g oil/cc soil)      0.00372
Enter Ci x 10^6   VO ppmw      210000
l,Depth (cm)              67
Total porosity            0.4
Air Porosity (default=0)    0.265
MW oil                    190
VO diss. in water, enter 1   0
Time of calc. (days)        0.25
Biodegradation, enter 1      0
Temperature (Deg. C)         17
Wind Speed (m/s)             3.2
Area (m2)                    21.00
  
```

COMPOUND NAME	LANDTREATMENT EMISSION RATES (g/cm2-s)				
	TIME (hours)				
	0.25	1	4	12	48
GASOLINE	5.52E-07	2.76E-07	1.38E-07	7.98E-08	3.99E-08

COMPOUND NAME	LANDTREATMENT FRACTION LOST		INTERMEDIATE TIME 0.25 days	
	AIR	BIOL.	AIR	BIOL.
GASOLINE	1.000	0.000	0.093	0.000

Figure 1. Sample CHEMDAT6 Input and Output Data

GASOLINE IN SOIL MATRIX Estimated vs. Measured NMHC Emissions

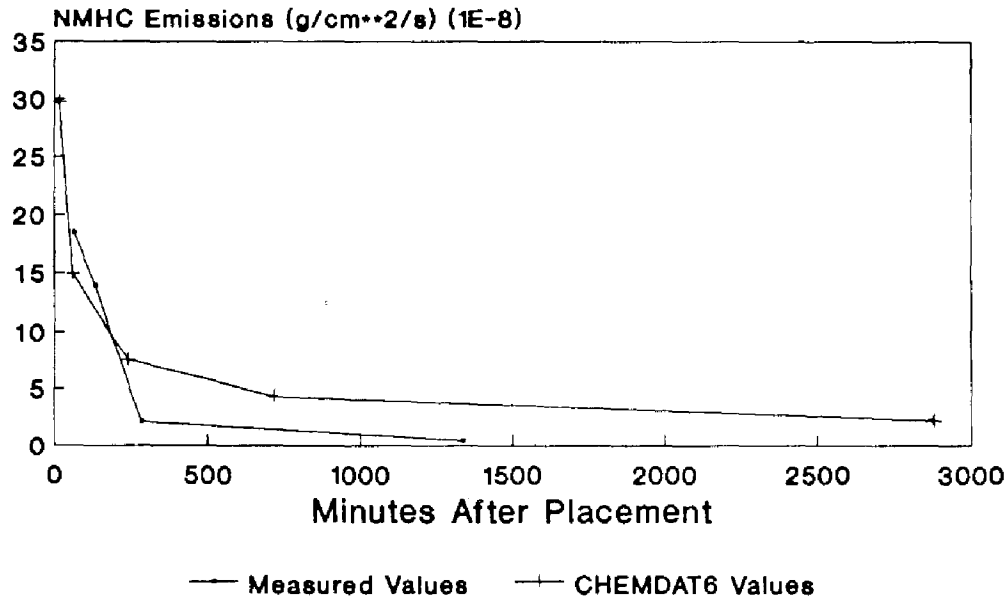


Figure 2. Plot Showing Estimated vs. Measured NMHC Emissions

TEN-HOUR EMISSIONS Estimated vs. Measured NMHC Emissions

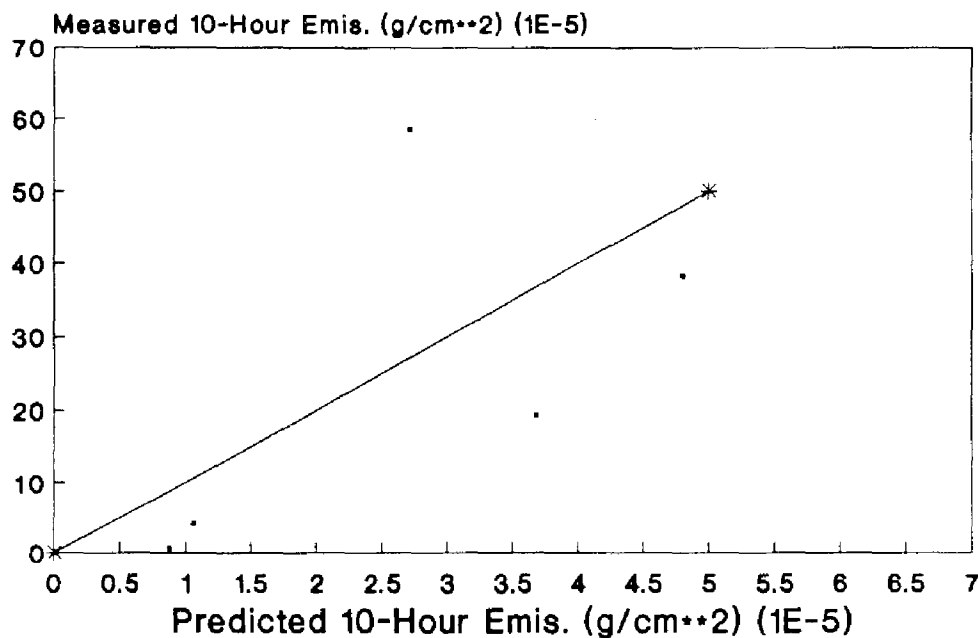


Figure 3. Scatter Plot Showing Correlation Between 10-hour Estimated vs. Measured NMHC Emissions

TEMPERATURE-CORRECTED DISPERSION MODELING OF
VOLATILE EMISSIONS FROM HAZARDOUS WASTE SITES

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A modification to the Industrial Source Complex-Short Term (ISCST) model is proposed to provide the option of correcting volatilization source terms, on an hourly basis, in proportion to the variation in vapor pressure that results from the diurnal temperature cycle. Measurements are presented to demonstrate that air temperature, a standard meteorological input parameter, is a suitable surrogate for surface soil temperature, a more direct determinant of volatilization from the surface. The derivation of the proposed correction term is described, and results from test runs of the temperature-corrected and the standard model are compared. Diurnal variations in relative flux, plume dilution, and predicted ambient concentrations are presented. The effect of this correction on annual concentration estimates is shown for five compounds.

Annual concentration estimates are 200-300% lower when the hourly correction option is selected than when a constant flux, determined for a reference temperature of 25°C is used. In addition, maximum hourly concentrations, predicted to occur (contrary to popular belief) during nighttime stable conditions, were 50% lower with the temperature-corrected model than with the standard version.

Introduction

Air pathway assessment of volatile organic emissions from hazardous waste sites involves two distinct steps: 1) determining the volatilization flux and 2) dispersion modeling to determine exposures to people living off-site. Emission fluxes are commonly either estimated by one of several exposed-waste volatilization models or measured. In either case, the source term is often determined at daily maximum temperatures and then assumed to be constant for the entire 24-hour day (and often, for the entire year). However, by examination of the models recommended for estimating volatilization from waste surfaces¹, it can be seen that volatilization flux varies in proportion to the saturated vapor pressure, which in turn varies with temperature. Thus, for example, for a typical summertime, diurnal temperature range of 15-33°C, (Boise, Idaho in July²), the vapor pressure of toluene, a moderately volatile compound, ranges from 16 mm Hg at night to 39 mm Hg during midday, a 240% increase, and the volatilization flux is expected to increase proportionately.

Atmospheric dilution also varies throughout the day, however. The gaussian plume equation for a ground-level point source³,

$$C = \frac{Q}{\pi u \sigma_y \sigma_z} \quad (1)$$

indicates that the downwind ambient air concentration, C, is directly proportional to the source emission rate, Q, and inversely proportional to the product of the wind speed (u) and the horizontal and vertical dispersion coefficients (σ_y and σ_z , respectively). During very common, light-wind, clear-sky, summertime conditions, atmospheric stability ranges from very stable at night (F stability) to very unstable during midday (A stability). By reference to the A and F curves on the familiar Pasquill-Gifford σ_z and σ_y charts³, it can be seen that at 100 m downwind the product $\sigma_y \sigma_z$ is 5.6 m² for F stability (typically at night) and 300 m² for A stability (typically during midday). Thus, although the source term is 240% greater at midday, the atmospheric dilution (with constant windspeed) is 53 times greater, and the net effect is that ambient air concentrations during the day may be only 1/22 of those that occur during the night. Furthermore, both effects are driven by solar heating and therefore always occur together. Only by accounting for each effect simultaneously, on an hourly basis, can realistic diurnal variations be obtained.

A modification to the widely used Industrial Source Complex-Short Term (ISCST) model is proposed to provide the option of correcting the source term in proportion to the change in vapor pressure between that at the reference temperature, at which the base source emission rate was determined, and that at the ambient air temperature as input for each hour from the standard meteorological data file. The derivation of the proposed correction term is described, and results from test runs of the temperature-corrected and the standard model are compared for a hypothetical 10 m x 10 m source area.

Methods

Soil versus Air Temperatures

The vapor pressure of an organic compound depends primarily upon the temperature of that substance at its volatilizing surface, rather than the temperature of the ambient air moving over it. To determine the

relationship between air and surface soil (or waste) temperatures, temperature sensors were installed 0.1 cm below the surface of a sandy/loam soil and in a shaded shelter one meter above ground level. The time history of hourly-averaged air and soil temperatures is presented in Figure 1. Surface soil temperatures are highly correlated with air temperatures during nighttime hours but become significantly warmer (5-20°C) during all but one midday solar heating period. The surface temperature cooled to below the air temperature on the sixth day after the soil was wetted. Therefore, at least during the critical nighttime periods of reduced mixing, this limited data set suggests that the ambient air temperature is a good surrogate for the surface soil or volatilization temperature of the organic waste under dry conditions and is conservatively cooler when the soil or waste is wet or rapidly volatilizing.

Temperature Correction Algorithm

The temperature dependence of saturated vapor pressure is shown, by the well known Clausius-Clapeyron equation, to be a function of the heat of vaporization. A wide variety of vapor pressure estimation methods have been derived by integration of the Clausius-Clapeyron equation. One of the simplest methods, with coefficients widely available, is a two-parameter version reported by Schlessinger⁴;

$$\log_{10} P = (-0.2185 A/T) + B \quad (2)$$

where P is the vapor pressure in Torrs, T is the temperature in degrees Kelvin, A (the "A coefficient") is the molar heat of vaporization in calories per gram mole, and B is a constant. The correction factor for scaling the source term in proportion to the relative vapor pressure can be written by solving Equation 2 for the vapor pressures at the ambient (P_{amb}) and reference (P_{ref}) temperatures (T_{amb} and T_{ref} , respectively) and substituting both into the ratio P_{amb}/P_{ref} . The final temperature correction factor, TCORR is thus obtained;

$$TCORR = \frac{P_{amb}}{P_{ref}} = 10^{[0.2185 A (1/T_{ref} - 1/T_{amb})]} \quad (3)$$

where the correction term requires only the reference and ambient temperatures and the molar heat of vaporization for the compound of interest.

The ISCST model was modified, by addition of two self-contained subroutines, to allow optional interactive selection of the compound or vapor pressure of choice from a menu listing compounds most frequently found at Superfund sites. The reference temperature, at which the base emission rate was measured or calculated, is entered by the user, and ambient air temperatures are read from the sequential hourly meteorological file as usual.

Dispersion Modeling

The modified program was exercised for five compounds over a range of vapor pressures to show the influence of this modification on model estimates. One year of sequential hourly meteorological data from Denver Stapleton Airport was used. In all cases, a unit emission flux (1.0 ug/m²-s) was assumed to emanate from a 10 m by 10 m ground-level source area

at a reference temperature of 25°C. Concentrations were computed at 100 m from the source edge for every 2-degree wind direction interval from 0 to 359 degrees.

Results

The model was initially exercised without the temperature correction. The maximum 24-hour concentration occurred on a fall day (October 25) with 11 hours of F stability and an average temperature of 7°C. When the temperature correction option was selected, the maximum 24-hour concentration occurred, more realistically, on a summer day (June 6th), with an average daily temperature of 18°C and 6 hours of F stability. The diurnal temperature variation and relative plume dilution variation for June 6 are shown in Figures 2a and 2b, respectively.

Three alternative source-term, temperature-correction assumptions for toluene are depicted in Figure 2c. Curve A represents the relatively common practice of estimating (or measuring) emissions at the daily maximum temperature and assuming that emissions are constant at that rate throughout the day. A somewhat more realistic option is to compute emission flux at the daily average temperature and keep it constant throughout the day, as indicated by curve B. Finally, by selecting the proposed hourly temperature correction option, hourly air temperatures are used to most realistically compute emissions for each hour (curve C).

As occurs on most days, the atmospheric stability on June 6 ranged from F at night to A just after noon, resulting in model-predicted relative dilution (at 100 m downwind) that is 39 times greater at midday than at night, as shown in Figure 2b. When the emission scenarios for the three described temperature correction alternatives are modeled with ISCST, the resulting ambient toluene concentrations, shown in Figure 2d, are obtained. Remarkably similar curves are reported by Harper, et. al.⁵ for pesticide volatilization. Although these three source treatments result in comparable concentrations during midday, fairly large differences occur at night, with the hourly-corrected concentration reaching only 50% of the "daily maximum temperature" case and 70% of the "daily average temperature" case.

It should be remembered that the measured surface soil temperatures ranged from 10°C cooler, with wet soils, to nearly 20°C warmer than the air temperature during midday. If the hourly corrected air temperature is increased by 20°C to simulate hot, dry surface soil temperatures, the ambient concentration increases insignificantly, as indicated by the single data point shown at 1300 on Figure 2d.

Perhaps the most striking conclusion to be drawn from Figure 2d is that the maximum hourly concentration occurs during the night and is 16 times greater than the maximum midday concentration. This result demonstrates that, contrary to popular belief, "high event" or worst-case conditions for air impacts from volatilization sources are during clear-sky evenings or nights when the atmosphere is most stable and temperatures are moderate, rather than during sunny, warm, midday conditions. This conclusion is supported by the fairly common observation that odor complaints at landfills, waste sites, and wastewater treatment facilities greatly increase during the evening and early morning hours.

Annual concentrations for the standard and temperature-corrected versions for five compounds are shown in Table I. Concentrations predicted by the corrected model are 200-300% lower than concentrations estimated using the standard (un-corrected) ISCST model. The greatest effect (300% lower) is seen for the lowest-volatility compound. In addition, the greatest effect is expected for continental climates with large diurnal temperature ranges, with the utility of this approach diminishing for coastal areas with small diurnal temperature ranges.

Conclusions

On the basis of limited air/surface soil temperature measurements and a theoretically based correction to the ISCST dispersion model, it may be concluded that 1) air temperatures serve as a good surrogate for surface soil temperatures when critical, low-dilution conditions occur; 2) annual concentrations are 200-300% lower, for Denver airport meteorology, when the hourly correction option is selected; and 3) the temperature-corrected model appears to provide more realistic diurnal and seasonal variation in ambient concentrations resulting from surface volatilization sources.

Finally, we would recommend that reference temperatures always be reported along with calculated or measured emission estimates. In addition, this analysis demonstrates that nighttime conditions should not be neglected when conducting "high-event" sampling or modeling for Air Pathway Assessment of surface-contaminated waste sites.

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5. L. A. Harper, A. W. White, R. R. Bruce, A. W. Thomas, R. A. Leonard, "Diurnal trifluralin volatilization flux," J. Environ. Qual. 5: 236 (1976).

Table I Annual Modeling Results

Denver Airport Meteorology
(base flux = $1.0 \mu\text{g}/\text{m}^2\cdot\text{s}$ @ 25°C for all cases)

<u>Compound</u>	<u>Heat of Vaporization (cal/gm-mole)</u>	<u>Vapor Pressure at 25°C (mm Hg)</u>	<u>Maximum Annual Concentration ($\mu\text{g}/\text{m}^3$)</u>
No correction	N/A	N/A	0.0393
1,3-Butadiene	5,688.2	1,848.7	0.0221
Chloroform	7,500.5	172.0	0.0189
Toluene	8,580.5	26.8	0.0173
Dichlorobenzene	10,446.8	2.3	0.0153
2-Hexanol	12,386.5	2.5	0.0133

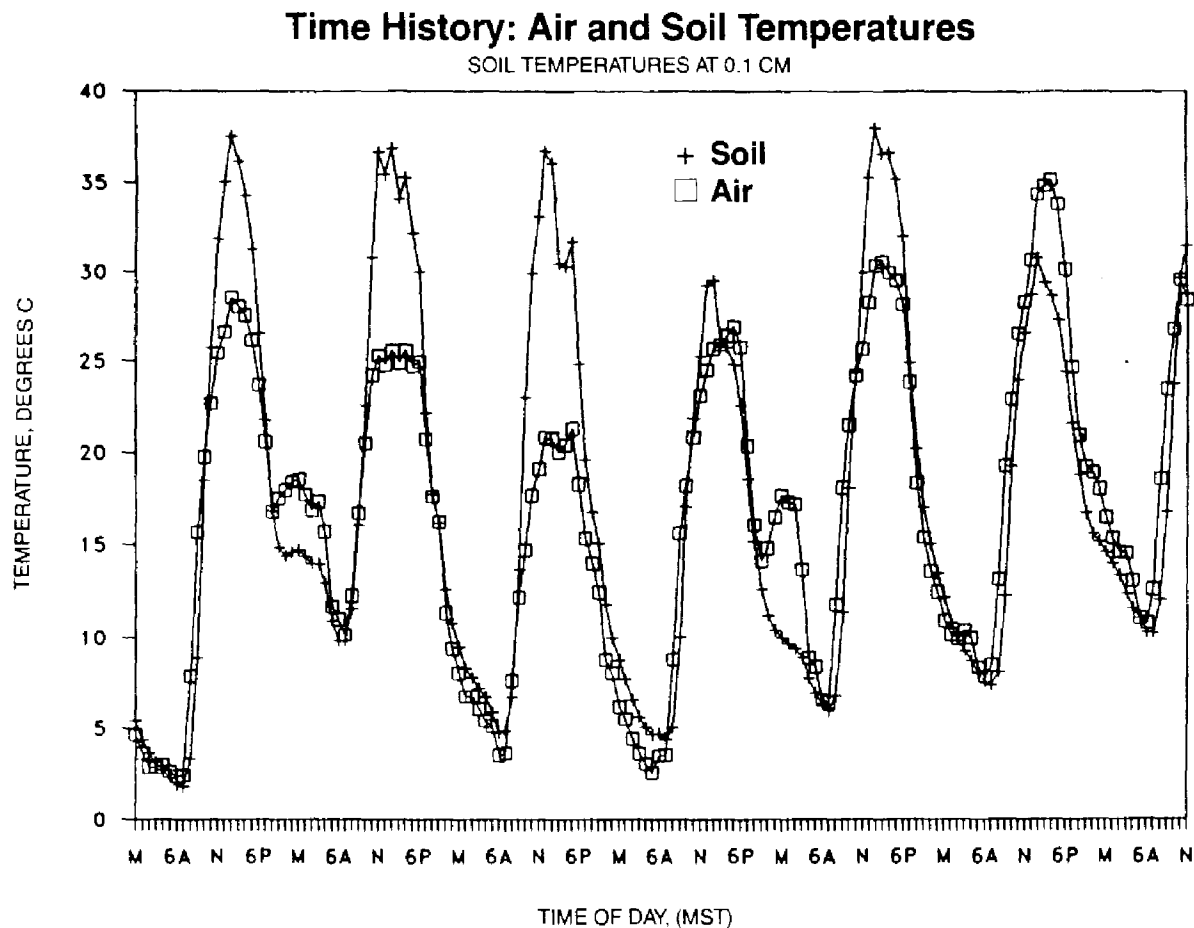


Figure 1. Time history of air and surface soil temperatures, April 10 - 16.

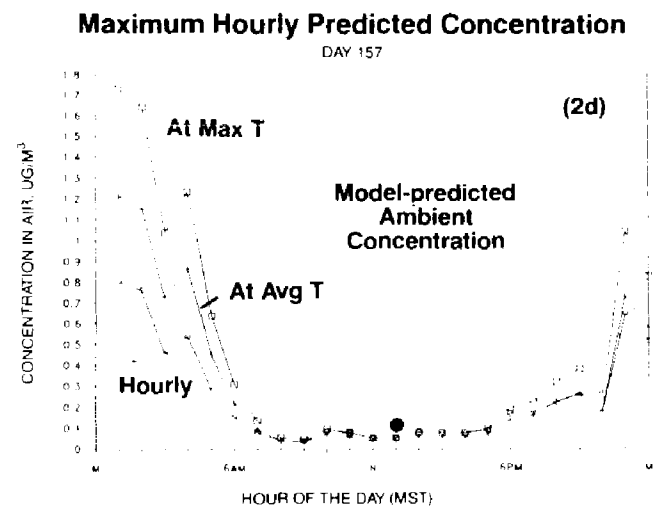
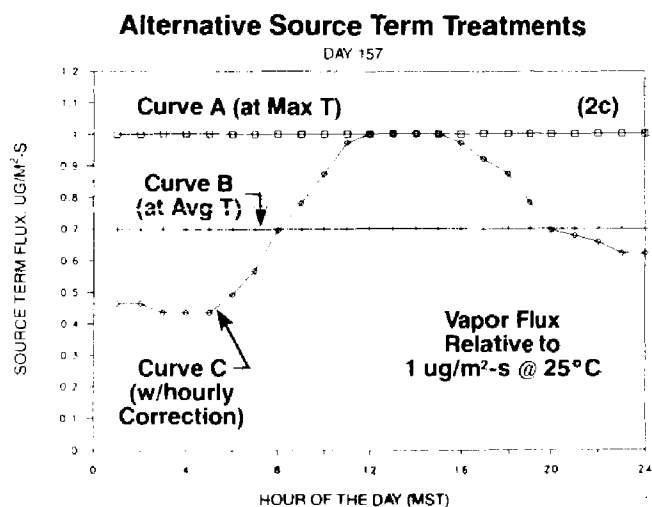
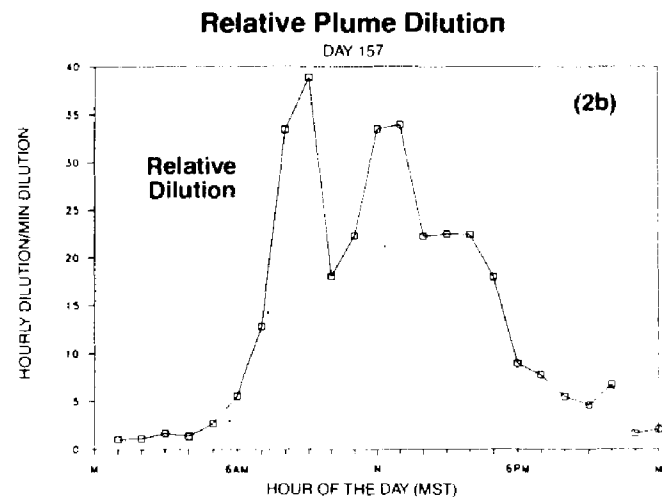
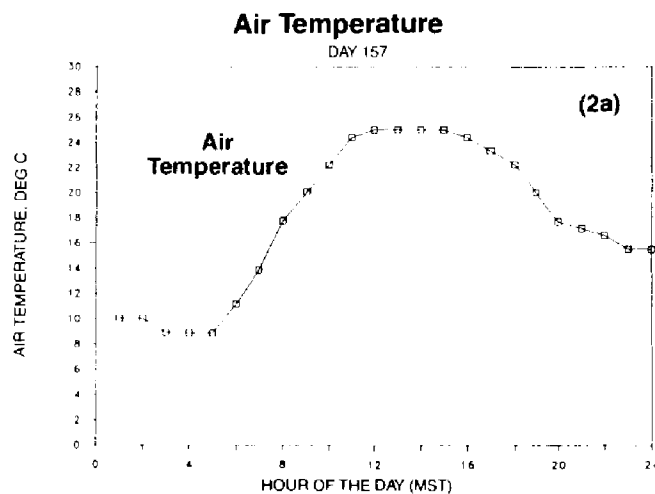


Figure 2. Diurnal variation in (2a) air temperature, $^\circ\text{C}$; (2b) plume dilution, relative to lowest dilution observed (= 1) at 0100 hrs; (2c) source volatilization flux, based on $1.0 \mu\text{g}/\text{m}^2\cdot\text{s}$ toluene flux at 25°C and assuming three alternative temperature correction approaches, $\mu\text{g}/\text{m}^2\cdot\text{s}$; and (2d) ambient air concentration ($\mu\text{g}/\text{m}^3$), resulting from three temperature correction alternatives shown in (2c), June 6, 1964, Denver Colorado Airport Meteorology. The data point (\bullet) at 1300 hours ($0.13 \mu\text{g}/\text{m}^3$) in figure 2(d) represents the concentration predicted at the midday air temperature (25°C) plus 20°C .

THE EFFECT OF WOOD FINISHING PRODUCTS ON INDOOR AIR QUALITY

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The use of stains, polyurethane finishes, and waxes on interior surfaces can cause elevated levels of vapor-phase organics indoors. Studies were conducted in an IAQ (Indoor Air Quality) test house to determine the magnitude and temporal history of indoor concentrations of organic compounds due to the use of these products. An oak floor was constructed and stained. The concentrations of total organics and certain individual compounds were measured at two locations in the house for a period of about 2 weeks. After 10 days, including 2 days of house ventilation, the same procedure was followed for a polyurethane finish. Finally, a liquid wood-floor wax was used and similar measurements conducted. During each test period, house air exchange rates were measured using a CO tracer. The measured concentrations of organics were compared to results obtained from an IAQ model (INDOOR): good agreement was obtained. The model used emission rate data developed from small chamber tests of the same products and the measured air exchange rates. The model also included an evaluation of adsorption to and re-emission from interior "sink" surfaces. The studies showed that re-emission from the sinks was the dominant factor affecting the indoor concentrations from 2 days after application to the end of the test period.

Introduction

A major objective of the EPA's IAQ program at the Air and Energy Engineering Research Laboratory is to determine the impact of sources on IAQ. An integrated research program involving chamber investigations, modeling, and test house studies has been developed to meet this objective. The program involves the development of emission factors, research to develop models to analyze the impact of the emissions on IAQ, and studies in an IAQ test house to verify the model predictions. This paper describes how this three-phase approach was used to evaluate the impact of three wood finishing products (wood stain, polyurethane, liquid wood-floor wax) on IAQ.

Experimental Methods

Small Chamber Studies

Methods for determining emission characteristics of a wide variety of indoor sources using small test chambers have been developed.¹ A known quantity of clean air is passed through a chamber containing the indoor source to be evaluated. The chamber outlet concentration of vapor-phase organics is measured over time using appropriate sampling techniques followed by gas chromatographic analysis. Emissions of both total measured organics and individual compounds are reported. The resulting concentration vs. time curve is then analyzed to determine the emission rate for the source. The emission rate is generally reported in the form:

$$ER = ER_0 e^{-kt} \quad (1)$$

where ER is the emission rate at time t, ER_0 is the initial emission rate, and k is the decay constant. The three products discussed herein were tested in this manner.

IAQ Test House Studies

EPA operates an IAQ test house that is used for experiments to provide measurements of the effect on IAQ of sources in full-scale indoor environments. These measurements are used to validate the small chamber emission rates and to verify an IAQ model (see below). The floor plan for the test house is shown in Figure 1.

This paper reports on a set of experiments designed to determine the effects of three wood finishing products on IAQ. An oak floor (2.44m x 2.44m = 5.95 m²) was constructed and placed in the test house dining area (see Figure 1). In the first experiment, a wood stain was applied to the floor, and the concentrations of total organics and certain individual compounds were measured at two locations in the house (living room and corner bedroom) for a period of about 2 weeks. Samples were collected on Tenax/charcoal sorbent tubes. The tubes were thermally desorbed and analyzed by a gas chromatograph equipped with a flame ionization detector. Each test period was followed by a waiting period of about 10 days, including 2 days for house ventilation. The same procedure was followed for a polyurethane finish. Finally, a liquid wood-floor wax was used and similar measurements conducted.

During each test period, house air exchange rates in air changes per hour (ACH) were measured using carbon monoxide (CO) as a tracer. The CO was released in the hall, near the return air vent, and monitored in the hall and de

IAQ Model

An IAQ computer model, INDOOR, has been developed to calculate indoor pollutant concentrations based on source emission rates, room-to-room air movement, air exchange with the outdoors, and indoor sink behavior.

Source Emission Rates. The emission rates of solvent based sources like those used in the test house experiments include an application phase and a decay phase. INDOOR uses the following expression to calculate the total emissions:

$$ER_{tot} = ER_{app} + ER_0 e^{-kt} \quad (2)$$

where ER_{tot} is the total emission rate and ER_{app} is the emission rate during the application phase, t_{app} .

Sink Adsorption and Re-emission. Research has shown that sinks (i.e., surfaces that adsorb and re-emit indoor pollutants) play a major role in determining indoor pollutant concentrations. INDOOR uses the following model to describe the behavior of indoor sinks:

$$dM/dt = k_a C_t A - k_d^* (M_t)^n A \quad (3)$$

where dM/dt is the rate of change of mass in the sink, k_a is the adsorption rate constant, C_t is the indoor pollutant concentration at time t , A is the area of the sink, k_d^* is the desorption (re-emission) rate constant, M_t is the mass in the sink at time t , and n is an empirical constant.

Results

Figures 2, 3, and 4 present the results of the three test house experiments. Each figure shows the concentration of total organics measured in the living room of the test house over the course of the experiment. The figures also provide two model predictions based on the input data shown in Table I. The emission rate data in Table I are based on small chamber studies of the three products.

Table I. Input Values for IAQ Model Predictions

Variable	Wood Stain	Polyurethane	Floor Wax
E_{app} (mg/m ² -hr)	12,000	12,500	58,000
t_{app} (hr)	0.4	1.5	0.1
ER_0 (mg/m ² -hr)	17,000	5,000	10,000
k (hr ⁻¹)	0.4	0.25	1.0
ACH (hr ⁻¹)	0.3	0.36	0.4

The "No Sink" predictions were made by assuming that the interior surfaces of the test house did not adsorb or re-emit organic vapors. The IAQ model predictions assumed that the interior surfaces behaved as described by equation (3), with $k_a = 0.2$, $k_d = 0.003$, and $n = 1.5$.

The figures show that concentrations of total vapor-phase organic compounds much greater than 100 mg/m^3 were obtained when the three high solvent content wood finishing products were used indoors. The figures also clearly indicate the effect of indoor sinks on the time history of the concentration of vapor-phase organics. The "No Sink" predictions show that, in the absence of sinks, the concentrations would drop to background levels within 2 days of using any of the wood finishing products that were evaluated. The test house data and the IAQ model predictions provide evidence that adsorption to and re-emissions from the sinks in the test house impact the indoor concentrations for up to 2 weeks after product usage.

In general, the IAQ model predictions fit the data for all runs quite well. Some of the lack of fit between the model and the data is due to varying air exchange rates over the course of the experiment caused by changing weather conditions, while the model uses a constant air exchange rate. The model is being modified to allow the air exchange rate to be varied. The fit could also be improved by using different sink constants for the different sources and sink materials. However, until knowledge of and data on the behavior of sinks are improved, this modification is not possible.

Conclusions

A three-phase approach involving small chamber studies, IAQ test house experiments, and IAQ modeling was used to investigate the effect of wood finishing products on indoor concentrations of vapor-phase organic compounds. The experiments showed that indoor concentrations in excess of 100 mg/m^3 of total vapor-phase organics can occur after the use of such products. The importance of indoor sinks on the time history of the indoor levels of organics was demonstrated.

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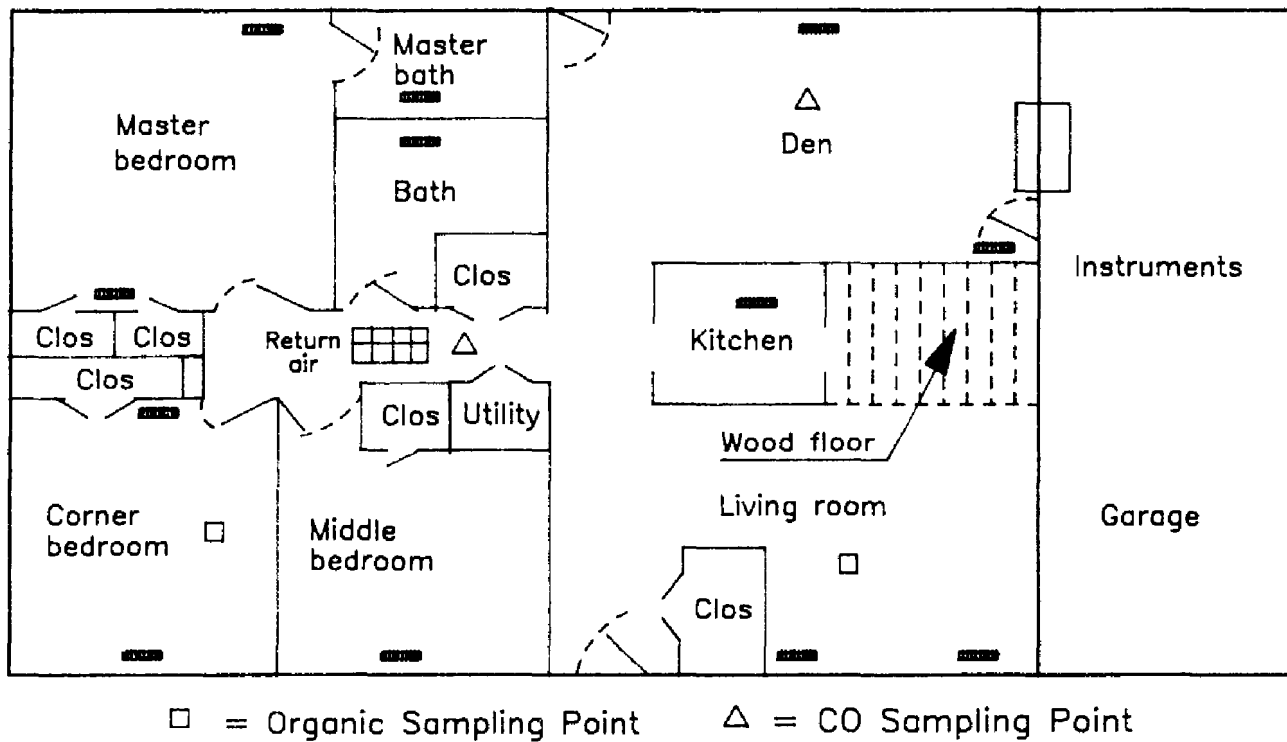


Figure 1 — IAQ Test House

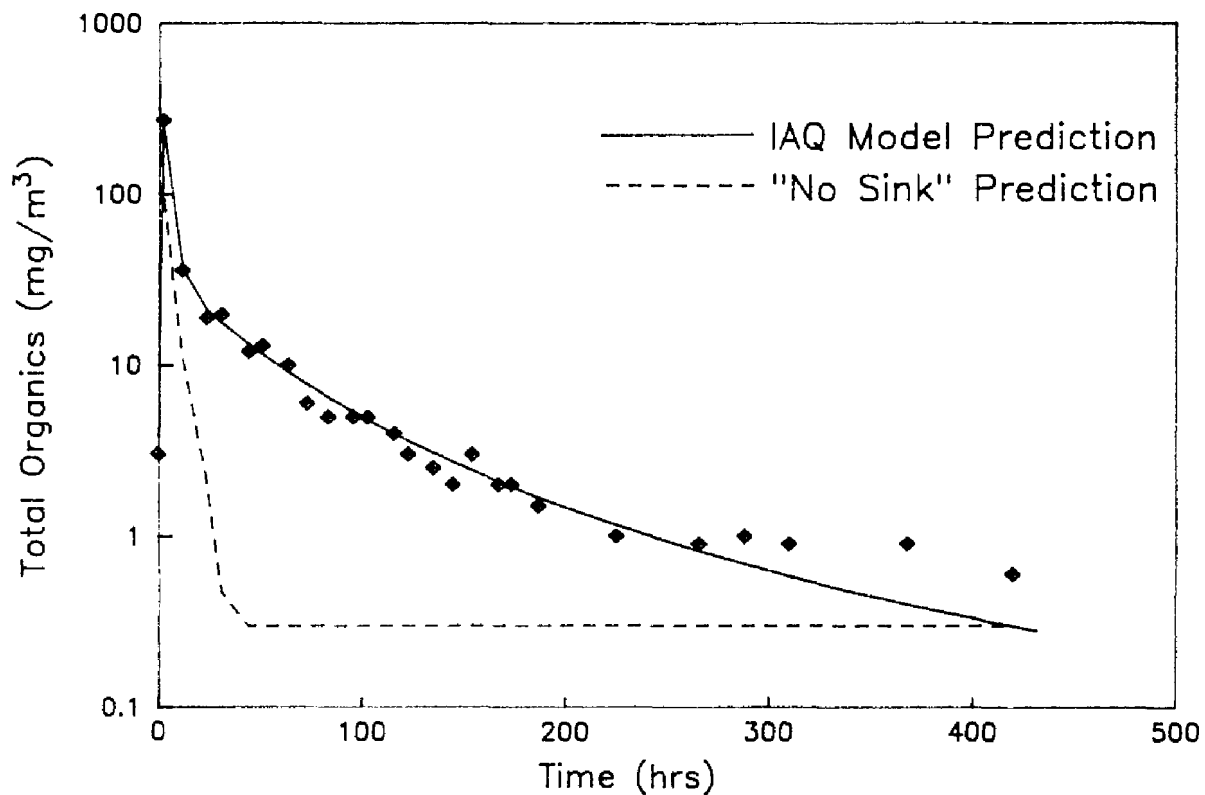


Figure 2 — IAQ Test House Experiment: Wood Stain

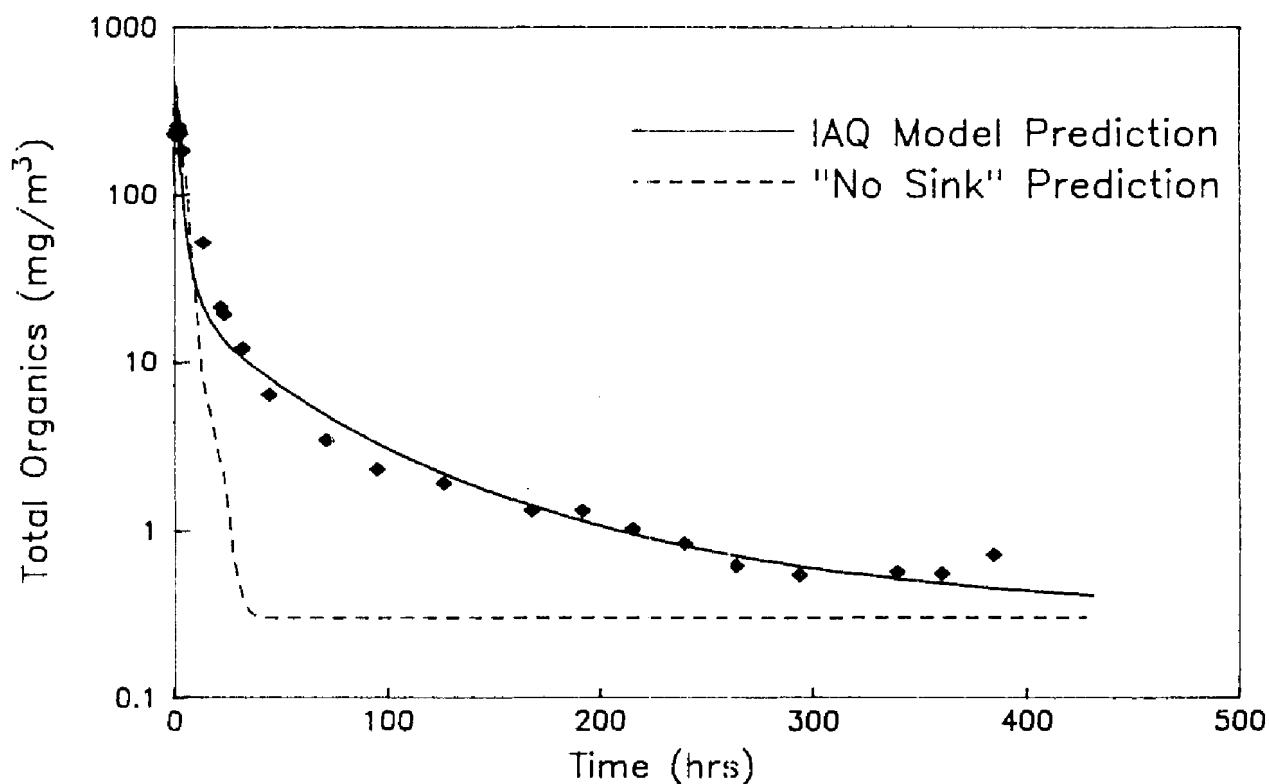


Figure 3 – IAQ Test House Experiment: Polyurethane

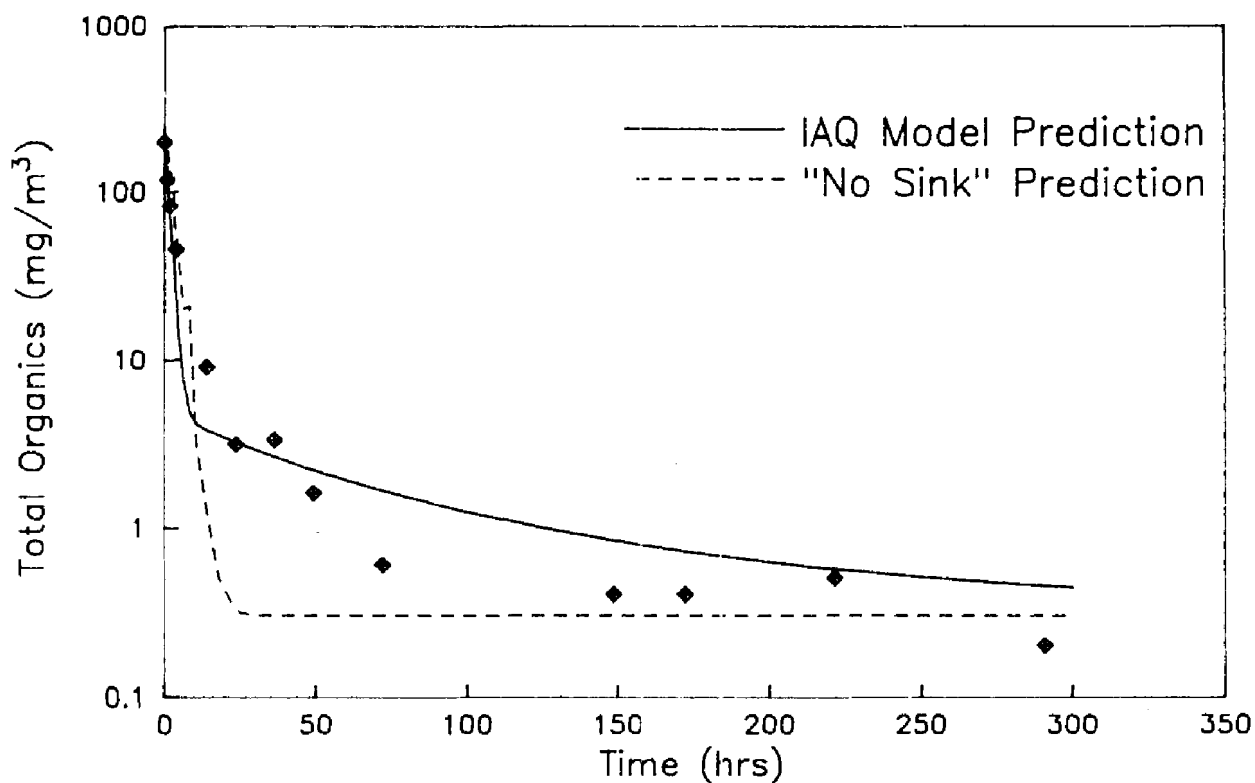


Figure 4 – IAQ Test House Experiment: Wood Floor Wax

INDOOR AIR TESTING FOR LOW-LEVEL VOLATILE ORGANICS:
A SITE-SPECIFIC TECHNICAL APPROACH

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Migration of subsurface contamination from industrial operations into neighboring residential structures raises concerns about possible human exposures and creates a demand for new technical approaches to assess exposure potential. This paper compares and contrasts the results from indoor air studies at two different sites to emphasize the importance of developing a site-specific technical approach to provide scientifically defensible and cost-effective assessments of exposure potential for the site, taking into account such factors as subsurface conditions, types and levels of contamination, other sources of contamination, and characteristics of the residential structures.

A technical approach is described that was used successfully to evaluate human exposures to potential subsurface contamination consisting of low levels of volatile organic compounds found in common household products and urban ambient air. The approach involved indoor air and outdoor ambient sampling in the study neighborhood, along with indoor and outdoor sampling in a control neighborhood where no subsurface contamination was present. State-of-the-art sampling and analytical techniques were used to measure part-per-billion levels of the target compounds. A comprehensive quality assurance/quality control program, including detection limit studies, was conducted to establish limits of certainty critical to data interpretation. The results of the study underscored the importance of this site-specific approach: Nearly all measured concentrations were less than 100 parts per billion, and the concentration differences were very low - often negligible - between indoor and outdoor air, and between the study and control neighborhoods.

Results from a second site are considered to demonstrate a different technical approach. In this case, the subsurface contamination consisted of indicator hydrocarbons at relatively high levels, with much higher concentrations measured indoors than in the outdoor ambient air or the control area. Comparison of the results from the two sites suggests that unique study design criteria are often dictated by relatively subtle differences in site factors.

Introduction

Migration of subsurface chemicals from industrial operations into neighboring residential structures can present the potential for human exposures to indoor airborne chemicals. This paper presents the results of exposure assessments conducted in two residential neighborhoods, each located adjacent to an industrial facility where subsurface chemicals had been measured and could potentially impact indoor air quality in the residential structures. Although the sites and study objectives were quite similar, different site-specific technical approaches were required to provide technically defensible, conclusive data in a cost-effective manner. The following discussion demonstrates how these technical approaches evolved in response to preliminary findings, regulatory agency requirements, community concerns, and the industrial facilities' philosophies.

Background

Site 1 was an ocean-front residential neighborhood bordered on one side by a large refinery. Subsurface contamination consisted of liquid petroleum hydrocarbon product that had leaked from several large storage tanks, creating a floating lens on the ground-water table. Volatile components had been measured in the shallow soil vapor in the neighborhood at levels up to 10,000 ppmv total hydrocarbons (THC) in one area. Types and relative concentrations of hydrocarbons were characteristic of an intermediate petroleum product; predominant species included C₃ and C₄ aliphatics, benzene, toluene, xylene, and various olefins. The outdoor ambient air was expected to reflect a significant ocean influence, since on-shore winds prevailed. Odors had been observed at likely points of subsurface vapor infiltration in some structures, and these were reported to the health agencies. Real-time screening with organic vapor analyzers equipped with flame ionization detectors (OVA-FIDs) in selected structures near the higher soil gas contours indicated high point sources (5000 to 10,000 ppmv THC) at likely points of infiltration, such as floor-wall joints and cracks or holes in floors or walls. Elevated THC levels (up to 100 ppmv) were also measured in the centers of rooms at approximately five-foot heights in some structures (referred to as "room ambient" locations).

The neighborhood was located in a very desirable area of expensive homes. Limited community organization or reaction was exhibited during the investigations. The regulatory agencies adopted a cooperative, "hands-off" approach, and much of the oversight was handled by local authorities during the investigation phases. Priorities shared by the refinery management and the regulatory agencies were expeditious completion of the investigative phases and prompt mitigation if needed.

Site 2 was a residential neighborhood located adjacent to a very large chemical manufacturing facility. The facility manufactures and uses a wide variety of common solvents, many of which had been measured in ground water on site. These compounds had not been measured in shallow ground water at the facility's fenceline; the highest concentrations were measured in deeper ground water. Soil vapor testing conducted in early phases of the investigation did not indicate a plume of chemicals in the soil gas off site. Outdoor air was influenced by typical urban sources and by certain high-use solvents from the facility. Dispersion modelling indicated that measurable concentrations (i.e., >0.010 ppmv) of some solvents could be present in outdoor air.

The manufacturing facility was the primary employer in the area, and consistent with their longstanding "good neighbor" image, maintained a high

level of community involvement during the investigations. The community reacted to the subsurface findings with significant concern, and several existing and new groups represented the public interest. These groups were highly involved throughout the studies; representatives and hired consultants reviewed workplans and reports and attended regular meetings with the public agencies. The regulatory agencies also were highly involved, maintaining day-to-day oversight during all field activities and providing detailed input on the technical approaches and experimental protocols. The agencies required a strict comparison approach rather than design based on chemical toxicity and placed a strong emphasis on the completeness and thoroughness of the investigations.

Site 1 Approach and Results

The purpose of the indoor testing program for Site 1 was to determine whether subsurface compounds had entered structures via the surrounding soils. The indoor testing program for Site 1 was initiated with expansion of the real-time instrument surveys to include many structures in the neighborhood. In total, 313 structures were surveyed over a period of roughly six months. The real-time survey results, especially any elevated room ambient or point sources at likely infiltration points, were used to prioritize structures for testing using additional methods. With input from the regulatory agencies, additional testing was conducted in structures near the subsurface plumes or where elevated real-time readings were obtained to help identify any structures requiring mitigation measures. Charcoal tube sampling over eight-hour periods was conducted to test for C_1 through C_{12} hydrocarbons at point source and room ambient locations. Evacuated stainless steel canister grab samples also were collected at point source and room ambient locations and were analyzed using gas chromatography with multiple detectors (flame ionization, photoionization, and Hall electrolytic conductivity) to speciate a wide variety of compounds and to help identify types and ratios of compounds in structures for comparison to soil vapor and ground-water sampling data. Limited sampling was conducted using similar techniques in a control structure located in an area removed from the subsurface contamination.

Results from the indoor testing ranged from very low concentrations similar to baseline levels (determined from trip blank samples) and control structure levels to significantly higher levels of compounds similar in type, level, and ratios to those measured in the subsurface sampling. Likely presence of subsurface compounds in some structures was indicated by: elevated real-time THC readings at room ambient or suspect point source locations; elevated THC or total non-methane hydrocarbon (TNMHC) levels in charcoal tubes, with dominant C_5 and C_6 species at relative concentrations characteristic of the subsurface mixture; and canister sample species common to the subsurface at levels above baseline and in similar ratios to those in subsurface samples. Results for certain structures appeared to be very similar, suggesting various categories of data. Data from structures in the "Level 1" category typically included real-time readings above 30 ppmv THC at room ambient readings, elevated hydrocarbon point sources, subsurface-type hydrocarbons at levels well above baseline concentrations, and tracer species at ratios common to the subsurface plume. Data from structures in the "Level 2" category included real-time readings between 10 and 30 ppmv at room ambient locations and elevated point sources or subsurface-type hydrocarbons. Structures not in the Level 1 or Level 2 categories typically did not exhibit elevated room ambient or point source measurements, and the types and levels of any hydrocarbons measured above baseline levels were not similar to those in the subsurface plume. Of the 313 structures, 4 fell into the Level 1 category, and 5 fell into the Level 2 category. Average concentrations of

some key species are presented in Table I, where the relationship between the types and levels of subsurface compounds and those measured in the indoor samples is demonstrated.

Level 1 structures were prioritized for mitigation. Short-term mitigation measures were developed in coordination with the regulatory agencies prior to startup of a vapor recovery system, which served as the long-term mitigation measure. Short-term mitigation activities included sealing and caulking floors, cracks, and holes that could serve as vapor infiltration points. Follow-up testing was conducted in these structures following the completion of the short-term mitigation measures, and additional follow-up testing was conducted after startup of the vapor recovery system.

Site 2 Approach and Results

Design of the indoor testing program for Site 2 was based primarily on the very low levels and common nature of compounds expected to be measured indoors, and on specific requirements of the regulatory agencies. As for Site 1, the purpose of the indoor testing was to determine whether subsurface compounds had entered structures through the surrounding soils. The target compound list was provided by the regulatory agencies and included eight relatively common solvents. Results of subsurface investigations indicated little or no likely influence on indoor levels. Some or all of the compounds were likely to be present in household chemical products and in the outdoor ambient air. In addition, three of the target compounds (benzene, toluene, and cyclohexane) had been measured in natural gas. Since most of the structures were supplied with natural gas for heating and hot water, this was another potential indoor source of the target compounds.

At the request of the regulatory agencies, the offer of testing was extended to every structure along the fenceline in the study area; 49 structures were tested over approximately six months. To provide data representative of typical residential levels of target compounds, control area testing was conducted. The control area was selected to be as similar to the study area as possible without the presence of any subsurface contamination. In selecting the control area, features such as age, size, value, construction, heating types, and garage types of the homes were considered, along with the predicted ambient air quality based on dispersion modelling. Twenty control area structures were tested to provide a representative data set that could be compared to the study area data set. Simultaneous outdoor testing was conducted at each study area and control area location to indicate outdoor levels of target compounds during the indoor testing.

Gas chromatography/mass spectroscopy was used to analyze eight-hour evacuated stainless steel canister air samples for the target compounds. In addition to the target compounds, the ten compounds producing the largest GC response were reported to further characterize the air samples. Real-time instruments were used to screen for point sources of natural gas or other point sources, and a complete inventory of household chemicals was performed while the samples were being collected.

Detection limit studies and a high level of quality assurance/quality control (QA/QC) testing were performed to evaluate the limits of certainty associated with individual low-level results. Results of these assessments indicated good performance of the sampling and analytical systems, and provided method and total system detection limits, along with measures of the inherent variability and false positive/negative potential that were