

Measurement  
of  
Toxic  
&  
Related  
Air Pollutants

PROCEEDINGS OF THE 1993 U.S. EPA/A&WMA  
INTERNATIONAL SYMPOSIUM

*Measurement of Toxic and  
Related Air Pollutants*

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## Preface

The 1993 United States Environmental Protection Agency/Air and Waste Management Association International Symposium, Measurement of Toxic and Related Air Pollutants was held in Durham, North Carolina on May 3-7, 1993. This annual symposium is sponsored by the United States Environmental Protection Agency (USEPA), Atmospheric Research and Exposure Assessment Laboratory of Research Triangle Park, NC, and the Air and Waste Management Association (A&WMA) of Pittsburgh, PA.

The four day technical program consisted of 190 oral papers presented in twenty four separate sessions plus a poster session with twenty papers. Individual sessions concentrated on recent advances in the measurement and monitoring of toxic and related air pollutants in the ambient atmosphere, in the indoor air of homes and highly confined spaces, and in emissions from stationary and mobile sources.

Course offered in conjunction with the symposium were taught by leaders in the field of air pollution monitoring and focused on basic sampling and analytical methodology. Exhibits were on display from sixty instrument and consulting services. The keynote address was presented by Allen Klmek, Director of Air Management of the Department of Environmental Health and Natural Resources of the state of North Carolina.

Measurement and monitoring research efforts are designed to anticipate potential environmental problems. Research supports regulatory actions by developing an in-depth understanding of the nature of processes that impact compliance with regulations and evaluates the effectiveness of health and environmental protection through the monitoring of long-term trends. EPA's Atmospheric Research and Exposure Assessment Laboratory 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. The Laboratory has the responsibility of implementation of a national quality assurance program for air pollutant measurement systems, and supplying technical support to Agency regulatory programs on local, regional, and global scale.

The A&WMA provides a neutral forum where environmental professionals share technical information about air pollution measurement and control. This year (1993) was the 13th consecutive year of the symposium and the 8th year of its co-sponsorship with the A&WMA.

Bruce W. Gay Jr. (USEPA)  
R.K.M. Jayanty (RTI)

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*Session 1*

*Radon Indoor Air Pollution*

## Evaluation of Radon Movement Through Soil and Foundation Substructures

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### ABSTRACT

To study convective and diffusive soil gas movement through soil and foundation substructures, a chamber (2 x 2 x 4 m long) filled with soil having an elevated radium content will be described. The chamber is filled with a soil of known characteristics such as radium and radon concentrations, packing density, and moisture retention properties. A depressurized perforated tube located in the center of the soil chamber will draw radon-laden air or a tracer gas through the soil and simulated building foundations under varying moisture conditions. Pressure contours and radon concentrations will be measured using an array of pressure sensors and radon extraction probes distributed within a two dimensional cross section extending the length of the chamber. Tracer gas transport rates from 23 probe sites to the center tube will also be measured. Data generated will be used to compute the soil permeability as a function of moisture in order to better understand radon transport in soils. The project will yield valuable information about how radon moves through soil and enters homes and will consolidate our understanding of other areas of research such as radon blocking and pressure and temperature driving forces. The scope of this paper is to describe the chamber, materials, instrumentation, and measurement methods utilized in this project.

### INTRODUCTION

#### System Description

To evaluate the movement of radon through soil and foundation substructures, a pilot scale chamber was designed to study the influences of several parameters (1, 2). To better understand the influence of certain entry routes on indoor radon and to design more effective countermeasures, a better understanding of the transport mechanisms is required. Mathematical models describing radon transport and entry have been developed; however, validation of the models is necessary through the simulation of transport processes under controlled conditions (3). To simulate conditions for the movement of radon gas through soil, a research chamber has been constructed containing 16 m<sup>3</sup> of soil with high levels of naturally occurring radium (averaging 6 pCi Ra<sup>226</sup>/g soil) which is able to generate elevated levels of radon (approaching 2000 pCi Rn<sup>222</sup>/l). Pressure-driven flow conditions will be monitored along a two dimensional plane intersecting the central length of the chamber (see Figure 1). Pressure differential, radon concentration levels, and air drawn through the soil from the surface will be measured. To simulate the flow of soil gas in the chamber a vacuum is created inside a perforated pipe line (suction tube), located across the center of the chamber, and another pipe located across the end at mid-depth of the chamber. These will provide the driving force for the convective flow of gas in the soil. The data generated, analysis, and interpretation of results are not addressed and will be covered separately.

## Chamber

The chamber is built from carbon steel sheet, 1.27 cm thick. The rectangular box measures approximately 4 x 2 x 2 m (LxWxH), with eight buttresses supporting the structure. The inside surface of the chamber and measurement probes are coated with latex paint as a corrosion inhibitor. The chamber sides are bolted (with 1.25 cm bolts), and joints are sealed with silicon, allowing it to hold approximately 33,000 kg of soil and water without leakage of water. Water used in the soil packing process and for its influence on radon emanation and gas transport, is adjusted by adding or draining. Three drain openings at the base are connected to three sight tubes and valves to allow for the adjustment of the water level inside the chamber. A spray bar sprinkler unit mounted above the chamber can also be activated if an increase in soil moisture is desired. Soil moisture is measured by use of a Troxler Sentry 200-AP moisture sensor which is described below.

## Soil

The soil used in the chamber was obtained from a phosphate mining area of Florida, and transported to the research facility at the Research Triangle Park, North Carolina. Eight samples were analyzed for radium content by the University of Florida, yielding an average of 4.85 pCi Ra<sup>226</sup>/g. Eleven samples were also analyzed by North Carolina State University, to determine soil properties, such as bulk density (averaging 1.636 g/cm<sup>3</sup>), saturated hydraulic conductivity (an average K = 31.698), and the soil content of components (averaging sand 97.38 percent, silt 0.96 percent, and clay 1.66 percent). Moisture retention properties were determined by equal weights of dry soil being packed at various densities and saturated by flooding, the deviation in bulk density exhibited by soil samples was minimal (less than 3 percent), indicating that the sandy soil would attain a similar density after saturation by flooding. The ability of this soil to attain near maximum density after saturation allowed for the chamber to be packed with careful attention given to areas surrounding the sampling probes, to eliminate air pockets.

## Soil Bed Construction for the Chamber

In excess of 20,000 kg of soil was used to fill the soil chamber, in incremental layers of 0.5 m, by the following procedure. First the soil was passed through a 1.9 cm metal screen to isolate debris and other foreign objects. The soil was evenly spread along the surface, and water was added to the sand until the water level was approximately 3 to 4 cm above the soil and allowed to settle for 2 days. The water was drained, soil density was measured (using the Troxler Nuclear Density Gauge, described below), and the next layer was added. Attention was given to ensure that the buried probes did not retain air volumes between the probe surface and the soil. Voids around probes could provide gases with a conduit for movement, which would cause inaccurate measurements of flow through the soil bed.

## Soil Moisture and Density

A nuclear density gauge was used to measure soil density during the soil bed preparation. An average of the measurements yielded a soil density of 1682 kg/m<sup>3</sup>. Each layer of soil loaded into the chamber was measured after flooding and draining: typically density values varied by plus or minus 5 percent. The moisture content of the soil material was measured using a Troxler Sentry 200-AP responding to changes in the dielectric constant of the material. The instrument utilizes a cylindrical probe that is lowered into a vertical access tube made from polyvinyl chloride (PVC) pipe (5.8 cm ID). By lowering the probe to varying depths, along this access tube, a vertical moisture profile of the soil bed can be established for the four locations of the access tubes in the soil chamber. An example of the moisture profile with soil depth in the chamber, as measured in four vertical PVC probes, is shown in Figure 2.

## Instrumentation

The sand filled chamber was instrumented with 23 sampling probes, which can continuously measure temperature and pressure and actively extract samples of soil gas by recirculating gas flow. During active recirculation and temperature measurement, the soil gas flows out of the tip of the probe and is drawn into the collar section. For pressure measurement, the pressure sensor is connected to the tip of the probe. Two suction tubes are buried approximately 1 m down in the sand (vertically central) and are used to provide depressurization to drive air flow through the soil. One suction tube is at the center of the box (horizontally

central) and one is at the end of the box. These tubes are divided into three sections: left, right, and center. Each section is attached to a valved vacuum pump, to provide the driving force for soil gas flow, and a pressure-sensing line. The same constant negative pressure is maintained in all three sections to isolate the center section from influences of edge effects arising from the finite dimensions of the chamber.

All three sections of the suction tube are automatically controlled to maintain the preset pressure by use of a mass flow controller for each section, and valved lines to correct for pressure imbalances. A separate pressure sensing system provides a safety valve to shut off the pressure source to prevent damage to the pressure transmitters in the event of over pressurization. The barometric pressure of the facility housing the chamber is measured with a Rosemont barometric pressure sensor, and sensors to indicate door openings of the test facility are used for two doors leading to the chamber laboratory. The sensitivity of the differential pressure cells used in all measurement probes requires a detailed accounting of all potential pressure influences. Barometric pressure and temporary pressure fluctuation (such as doors opening and closing) have been shown to influence chamber probe pressure measurements, and are considered when interpreting results.

The data collection system automatically records all pressure and temperature data from the 23 probes; the suction tube temperature; left, right, and center pressures; barometric pressure; the flow through the mass flow controllers; and the status (open/closed) of the front door to the test facility. It is necessary to monitor the operation of the outside door because the pressure disturbances are registered by the pressure sensors. Each of the 23 probes placed in the soil chamber is designed either to provide a point pressure measurement or to sample the soil gas (e.g., for radon concentration) with minimum interference to soil gas flow pathways leading to the suction tube. The spatial locations of the 23 probes are diagramed in Figure 3.

#### Chamber Operation

A vacuum pump pulls the soil gas from a large porous brass filter element near the end of the probe (diagramed in Figure 4). A manually operated, four-way valve is used to either a) recirculate the soil gas directly back into the box (to purge the lines) or b) direct the flow through a desiccating cylinder and scintillation cell (Lucas Cell) before being returned to the box. The upper and lower plenum dividers in the desiccating canister have been removed and the entire volume filled with desiccant (indicating anhydrous calcium sulfate) to reduce free volume in the system. After recirculating soil gas for a minimum of 20 minutes, at a flow rate of 0.5 l/min, soil gas flow is passed through the Lucas Cells for 4 min. Cells are then detached from the probe recirculation system and analyzed for radon gas according to "Protocol For The Determination Of Indoor Radon Concentration By Grab Sampling" (4). A series of experiments which were performed as part of this project were successful in optimizing the radon gas sample collection technique. However, a discussion of these experiments is beyond the scope of this paper.

An electrically operated, three-way valve isolates the differential pressure cell from the high pressure in the flow circuit to prevent damage to the cell. During operation, a J-type thermocouple monitors the flow temperature and is accurate to 0.25 °C. Differential pressure is measured with a Modus pressure transmitter. This capacitance type cell has an output range of 0 to 50 Pa with the accuracy of 1 percent of the range, and is selected to accommodate an expected differential pressure in the range of 15 Pa generated in the soil chamber.

### EXPERIMENTAL PLAN

Experiments have begun to measure changes in pressure, radon concentration, and temperature, when convective driving forces are applied. A vacuum of approximately 80 Pa is applied to the centrally located suction tube, and a flow rate of approximately 8 l/min is applied. Pressure and temperature are recorded over time from the moment of the initiation of the pressure. Within seconds the pressure change is recorded throughout the bed, from the probes closest to the suction tube to probes nearly 2 m from the suction tube along the central longitudinal plane. Radon gas grab samples are collected from each of the 23 probe locations, at a rate of approximately 14 samples in an 8 hour period (1 working day). Changes in radon concentrations take

10 to 20 days to reach a stable level. Tracer gas ( $\text{SF}_6$ ) times-of-flight are measured between the probes and the suction tube. The probe is used as the introduction point by injecting 10 ml of 100 percent  $\text{SF}_6$  by syringe, and analyzing the suction tube exhaust gases. The results characterize soil gas movement along the two-dimensional vertical plane dissecting the length of the soil chamber.

The chamber contains a second suction tube located near the end wall, to study the same effects described above on pressure and flow for distances up to 4 m between the suction tube and the most distance measurement probe. A simulated foundation substructure and stem wall (containing measured openings in joints) can also be incorporated into the chamber to study their influences on entry rates under defined conditions. The study of soil gas movement through greater distances of soil and possible obstructions to flow (such as foundation joints) is not part of the initial work, but is expected to be dealt with, and will be further discussed at that time.

### SUMMARY

A chamber was designed and constructed and experiments designed to characterize the movement of radon through soil and foundation substructures. Convective and diffusive flow conditions will be monitored along a two-dimensional vertical plane through the center of the chamber. Pressure, radon concentration, and temperature in the soil as well as tracer gas times-of-flight are measured. Mathematical models describing transport and entry have been developed; however, validation of the models is necessary. The project will yield valuable information about how radon moves through soil and enters homes. This paper describes the chamber, materials, instrumentation, and measurement methods utilized in this project. Data are currently being collected for analysis and interpretation and will be addressed elsewhere (5, 6).

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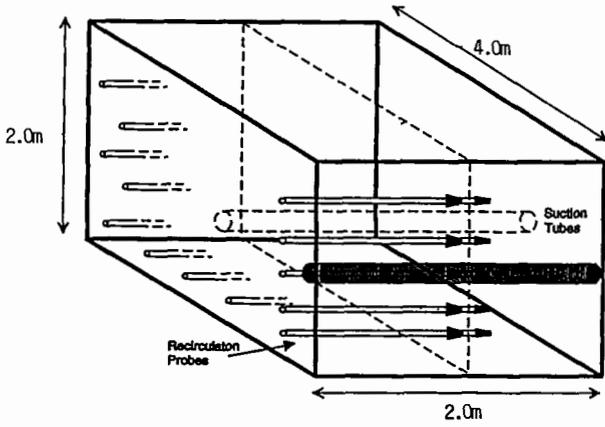


Figure 1. Chamber Probes and Suction Tubes

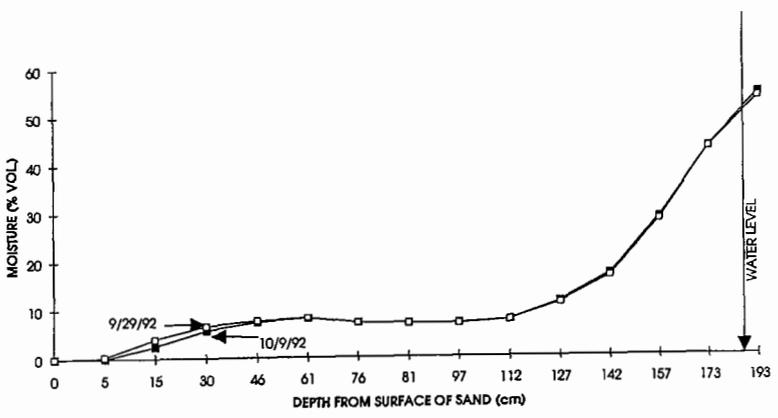


Figure 2. Soil Moisture with Depth

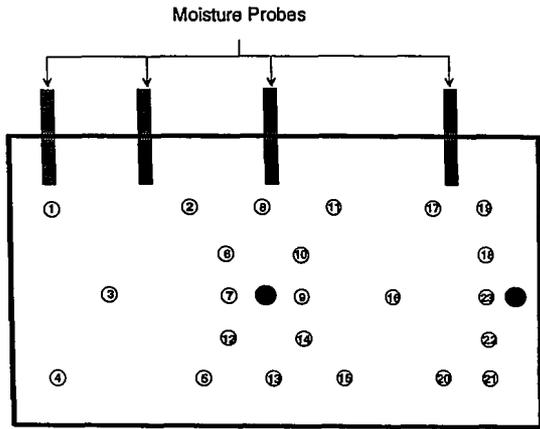


Figure 3. Radon Sampling and Moisture Probe Location (Chamber Side View)

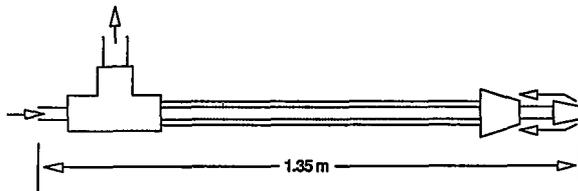


Figure 4. Sampling Probe

Comparison of Measurement Techniques for Soil  
Permeability in EPA's Soil-gas Chamber

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ABSTRACT

Initial measurements of soil permeability to the flow of air in EPA's soil chamber yield relatively good agreement between two methods. One method uses a set of 23 point probes located in a vertical plane of the chamber. These measurements are similar to the standard practice of measuring in situ soil permeabilities. The other method uses an arrangement designed to ensure ideal geometric flow patterns. It is argued that the latter measurement yields a better approximation of the effective bulk permeability that determines the advective flow through distributed entry paths into buildings such as cracks between floor slabs and walls. Measured moisture profiles in the soil are also discussed. The permeability measurements are compared to the predictions of a widely used empirical model.

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

Numerous field studies (1-4) have attempted to correlate measurements or estimates of radon concentration in the soil with measured radon concentration in the indoor air of buildings. So far, no one has provided a correlation with sufficient predictive strength to serve as a useful tool in projecting the severity of a potential indoor radon problem for a building yet to be constructed on a particular site. This lack of a strong correlation has usually been attributed to uncertainties in the properties of the soil at a given site and the uncertainties associated with the building structure and its entry paths.

However, researchers are beginning to question whether the fundamental assumptions and measurement techniques used to analyze the radon entry problem are adequate for certain types of soils. Researchers at Lawrence Berkeley Laboratory (5-8) have reported several instances in which conventional models underpredict both the entry rate of radon into structures and pressure fields in the surrounding soil. One proposed reason for these under-predictions is that the point probe measurement technique used to determine the permeability of soil-to-air flow may not adequately measure the appropriate soil property. The implication would be that the point probe does not necessarily measure the effective bulk permeability needed to describe flow that is distributed over extended entry routes.

In this paper, measurements of permeability obtained from a number of point probes will be compared with results from a system specifically designed to eliminate non-ideal effects on the flow field.

## SOIL CHAMBER

EPA's soil chamber was built to study the production and transport of soil-gas contaminants such as radon, pesticides, and landfill gases. The chamber is constructed inside a building in which the environmental conditions can be controlled. The chamber contains 16 m<sup>3</sup> of sandy loam from a phosphate mining area of Florida. The sandy soil was chosen largely to allow a uniform and isotropic prism of soil 2 m high, 2 m wide, and 4 m long. The chamber is designed to simulate full scale phenomena on the dimensions of a building, but only in two dimensions. A highly porous metal tube 0.05 m in diameter passes horizontally through the center of the prism. This tube can be used to simulate ideal flow toward a building feature such as a crack. The effects of the finite width (2 m) is compensated by the use of guard ends on the tube. The details of the chamber and its instrumentation are presented elsewhere (9,10). The key point is that the chamber is designed to sustain ideal flow between a large plane (the soil surface) and a long parallel cylinder. The bulk permeability of the uniform soil can be measured under these ideal flow conditions.

## SOIL MOISTURE

Soil moisture is measured using a Troxler Sentry 200-AP moisture monitor. The measurements are performed with a sensor inside a hollow polyvinyl chloride (PVC) tube installed vertically in the soil. The sensor measures the percent water by volume in the soil to an accuracy of 0.2% by measuring the effective capacitance of the soil under an applied electromagnetic field. Moisture profiles are generated by moving the sensor vertically inside the tube. Measurements are taken 0.15 m apart. There are four moisture measurement tubes in the soil chamber. Three tubes are in line on one side of the chamber at distances of 0.3, 1, and 1.5 m from the end of the chamber. The fourth tube is at 1.8 m on the other side of the chamber.

Moisture profiles, expressed as a percent of saturation for the four tubes, are illustrated in Figure 1. These profiles were all measured on the same day, but are hardly distinguishable from numerous sets of profiles measured periodically over 3 months. Moisture is hardly detectable in the top 0.2 m of soil. It then increases rapidly to about 15% and remains relatively constant to a depth of about 1.2 m where it begins to increase rapidly with increasing depth. The moisture reaches saturation near a depth of 1.75 m where the water level is located.

The permeability of the soil to air has been correlated to soil moisture by Rogers and Nielson (11). This relationship is illustrated by the solid curve in Figure 2. The permeability is relatively independent of depth (moisture) until the moisture reaches about 25% of saturation at which point the permeability decreases very rapidly with increasing moisture. The permeability decreases by 2 orders-of-magnitude by the time the soil reaches 80% saturation.

## PERMEABILITY MEASUREMENTS

This paper compares measurements of permeability using point probes with the effective bulk value measured with the system designed to eliminate non-ideal geometrical factors. However, the effects of varying moisture on the measured permeability is always of concern. Fortunately, for the present case, most of the flow occurs in the region of nearly constant permeability since the collecting cylinder is located 1 m deep.

The individual point symbols in Figure 2 represent measurements by individual point probes located in the central portion of the chamber near the location of the second moisture measurement tube. The solid line corresponds to the Roger's model for which the parameters were chosen to yield agreement with the bulk permeability in the region where permeability is constant. The dashed curve represents the same model adjusted to agree with the average value measured by the point probes in the region of constant permeability (near the surface). Qualitatively, the shape of the measured permeability curve resembles the model calculations. Note that the point probes indicate that the permeability decreases somewhat faster with increasing moisture

content than the Roger's model. Figure 3 compares the average measurement of all 23 probes with the Roger's model. The average values appear to emulate the model calculations somewhat more than the selected data of Figure 2, probably because of the reduced scatter. A measurement with an individual probe consists of 11 sets of pressure and flow values. The slope obtained from a linear regression of these values yields the measured permeability. The average standard error of the regression for all 23 probes was 2.6%. The maximum standard error for an individual probe was 4.4%. The 23 probe measurements are grouped at five depths represented by the square symbols in Figure 3. The two model calculations represented by the curves are the same as in Figure 2. The curve through the measurement points is provided to guide the eye, but has no implication as to shape or functional form. As before, the point probe measurements suggest that permeability decreases significantly at lower moisture levels than is indicated by the Roger's model.

Figure 4 shows the flow/pressure relationship from which the bulk permeability is computed. From equations 6 and 10 in reference (12)

$$k = \frac{\mu [0.764 + \ln(4h^2/b^2)] \text{ slope}}{4\pi L}$$

where  $k$  ( $\text{m}^2$ ) is the permeability,  $\mu$  ( $1.8 \times 10^{-5} \text{ kg m}^{-1} \text{ s}^{-1}$ ) is the dynamic viscosity of the soil gas,  $h$  (1 m) is the depth of the cylinder in the soil,  $b$  (0.0254 m) is the radius of the tube,  $L$  (0.666 m) is the length of the cylinder, and  $\text{slope}$  ( $1.60 \times 10^{-6} \text{ m}^4 \text{ s kg}^{-1}$ ) is the slope of the curve in Figure 4. The above equation yields a permeability of  $3.25 \times 10^{-11} \text{ m}^2$ . The average permeability measured by the point probes in the upper part of the soil is  $2.76 \times 10^{-11} \text{ m}^2$ . This value differs from the bulk value obtained from the slope of the curve in Figure 4 by only 15%.

#### DISCUSSION AND CONCLUSIONS

The interpretation of a measurement from a point probe requires some consideration. The term point probe is used merely to imply that the probe is small thus approximating a measurement at a point. The question, however, is to what extent does the measurement depend upon the exact geometry of the probe. The probes used in the current measurements were not true cylinders, but were actually truncated cones made of fritted brass. The slope of the sides of the cones was about 12 degrees. The analysis of the data treated the probes as cylinders with an effective diameter to yield the same surface area as the actual probe. Consistent with the common practice in field measurements, the geometrical factor associated with the probe assumed that the probe was quite long in contrast to the reality that its length is comparable to its diameter. This apparent inconsistency in analyzing the probe data gives rise to potential questions as to whether the close agreement (15% difference) with the bulk permeability may be somewhat fortuitous. The answer to this question may become clearer as future data are analyzed.

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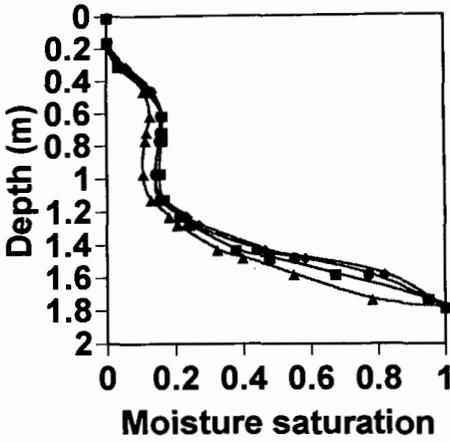


Figure 1. Measured fraction of moisture saturation at 4 locations.

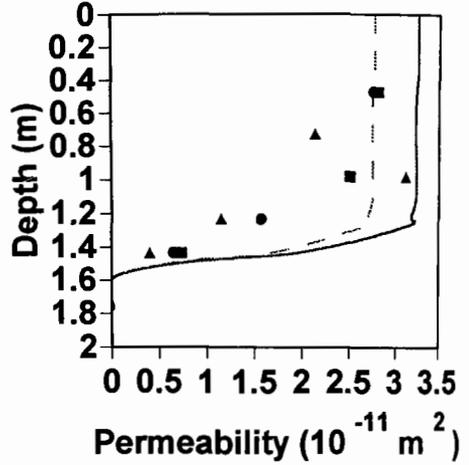


Figure 2. Comparison of measured and modeled permeabilities as a function of depth.

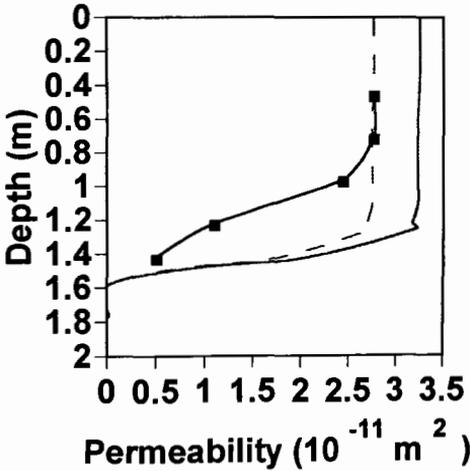


Figure 3. Comparison of the average measured permeability with model predictions.

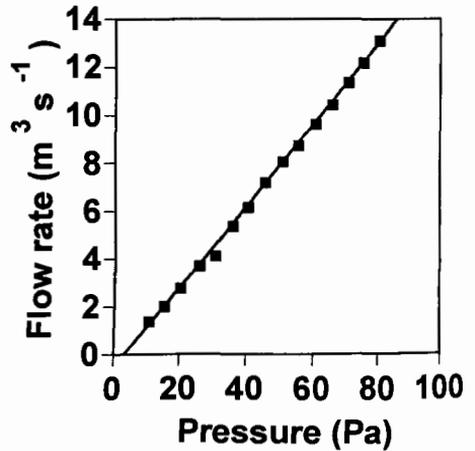


Figure 4. Plot of the total flow/pressure relationship.

## RADON IN FLORIDA LARGE BUILDING STUDY

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### ABSTRACT

This project is examining how radon concentration and indoor air quality levels are affected by building ventilation dynamics and building air system conditions, including mixing and leakage rates of typical residential, commercial, and public structures and heating, ventilating, and air-conditioning system components. The ventilation dynamics inherent to a building to dilute radon and indoor air pollution and overcome soil gas entry forces are being analyzed with the Florida Solar Energy Center computer model and diagnostic and mitigation protocols developed. Two research sites have had newly developed data collection stations and a weather station installed. Measurements of radon and carbon dioxide concentrations, temperature, humidity, and pressure within building zones and subslab areas, and outdoor air intake flow rates are being collected. The outdoor air intake will be adjusted from levels of no outdoor air to those recommended by the American Society of Heating, Refrigerating and Air-Conditioning Engineers (ASHRAE) as a modification of pressurization and dilution of indoor air conditions. Tracer gas active measurement injection and detection points were placed in all zones. Data from instruments are downloaded by computer modem connection to allow for prompt evaluation and analysis.

### INTRODUCTION

The objective of this project is to continue to develop, validate, and provide guidance for radon diagnostic procedures and mitigation strategies applicable to a variety of large buildings commonly found in Florida. To accomplish this, it was necessary to perform detailed field investigations and parametric studies in a variety of large buildings with elevated radon levels. The detailed investigations evaluate the nature of radon occurrence, building entry mechanisms, the effects of heating, ventilating, and air-conditioning (HVAC) system configuration and operation on radon entry, transport, and dilution, and the significance of HVAC configuration, occupancy patterns, building height, air passageways between floors, and other building construction features.

The majority of radon research in large buildings to date has focused on developing radon diagnostic and mitigation techniques for school buildings. Experience in other types of large buildings has been mostly

limited to new construction, rather than existing buildings. However, there are a number of similarities between school buildings and other similar sized buildings (i.e., construction methods, HVAC systems, building operation, and maintenance procedures). For this reason it is logical to believe that diagnostic and mitigation techniques developed by the U.S. EPA for schools can be used as the basis for developing diagnostic and mitigation techniques for other large buildings.

In accomplishing the project objectives the following activities have been included: 1) identification of candidate buildings, 2) selection of a representative sub-set of buildings for diagnostics and mitigation research, 3) developing standard radon diagnostic protocols applicable to large buildings, 4) conducting diagnostic measurements and research in selected buildings and 5) identifying building mitigation strategies based on the diagnostic measurements. Of these, only objectives 1, 2, and 4 have been accomplished at this point and are addressed in this paper.

## HVAC SYSTEMS

HVAC systems have two distinct primary functions: 1) the provision and maintenance of specific environmental conditions and 2) occupant or space ventilation for the provision and maintenance of acceptable indoor air quality (1, 2, 3, 4). Typically the specified environmental conditions are generally for occupant comfort, but can provide specific environmental conditions for a process or a product. In all cases the HVAC system must provide the occupant or process with the proper conditions (dry bulb temperature, relative humidity, air movement, etc.)(5).

The dominating feature of ventilation is the controlled introduction and removal of outdoor air (OA). Research indicates that the required amount of OA is dependent on the rate of contaminant generation and the maximum acceptable contaminant level. Understanding this is important to HVAC system designers since confusion can lead to designs that are energy wasteful (too much OA) or that provide poor indoor air quality (too little OA). For these two basic functions, there exist a wide variety of design situations. These include commercial and manufacturing applications, general office space, educational and institutional facilities, and special purpose space such as laboratories and clean rooms (6, 7, 8, 9, 10, 11 and 12).

## INSTRUMENTATION

This project is examining how radon concentration and indoor air quality levels are affected by building ventilation dynamics and building air system conditions, including mixing and leakage rates of typical residential, commercial, and public structures and HVAC components. The ventilation dynamics inherent to a building to dilute radon and indoor air pollution and overcome soil gas entry forces are being analyzed in an effort to develop diagnostic and mitigation protocols.

Large buildings, being complex in character, raise imposing demands on data needs. The significant demands of this project to measure many data parameters over time made it necessary to develop a new data collection station system. Measurements of radon and carbon dioxide concentrations, temperature, humidity, and pressure within indoor building zones, and subslab areas and outdoor air intake flow rates are being collected. The OA intake will be adjusted from levels of no OA to recommended ASHRAE levels (3) as a modification of pressurization and dilution of the indoor air conditions. Tracer gas was measured in all zones of both buildings studied. Weather station information is recorded continuously. Real time data from instruments are downloaded by computer modem connection to allow for prompt evaluation and analysis and minimize on-site time demands.

Measurements have been completed on one large building in Florida, and are nearing completion on

a second. The Financial Center North Building (FCN), located in Deerfield Beach, had seven data stations installed to measure radon, and carbon dioxide concentrations, temperature, humidity, differential pressure between indoor multiple zones, and subslab areas and the outdoor air pressure. In addition, OA intake flow rates and supply fan and exhaust fan discharge time of use were recorded. The OA intake was adjusted from zero to ASHRAE recommended levels of 20 ft<sup>3</sup>/min/person\*. PFT passive tracer gas emitters were placed in all rooms, and detector sets were placed in all zones for each OA intake level. Short term EPERM detectors were also used as integrated samplers for each outdoor air intake level.

Polk County Life and Learning Center (LLC) had five data stations and a weather station installed and made operational. All stations recorded the same type of data as that collected at FCN, and to improve data collection technique downloaded by phone modem.

For both buildings a certified test and balance (TAB) company was responsible for generating a list of system deficiencies (punch list) to be acted on by the building owner/operator, installing a flow control damper on the OA intake and balancing the HVAC system, and calibrating the damper. After all punch list items were corrected, the balance was adjusted and tracer gas was measured. Prior to each OA adjustment, EPERM measurements will be completed, and subslab grab radon will be measured. Tracer gas was measured in all zones to calculate interzonal mixing (four gases), and to calculate shell leakage and air exchange rate.

Both buildings had a total of five OA conditions (0, 5, 10, 15, and 20 ft<sup>3</sup>/min/person) tested for approximately 1 week each. Each week of testing will involve all three fan exhaust conditions( off, on and intermittent use), during which tracer gas will be measured. If air balancing is required with each OA condition, at the initiation of that condition the TAB will make these adjustments as soon as possible after the OA level is changed. During tracer gas testing all thermostat temperatures will be set within the comfort zone, and all doors will be closed to maintain supply air balance (it is anticipated that testing performed during weekdays cannot control door use due to normal facility usage). Data will be downloaded at least weekly and feedback on the success of measurement procedures to test all possible HVAC dynamic mechanisms will be communicated continuously.

## FINDINGS

The FCN building is a three-story office building that measures 46,000 ft<sup>2\*\*</sup>. The HVAC system is of the unitary system category having 23 separate air handlers (AHs), two OA intakes and contains office areas on three floors. The systems are fairly typical of speculative office space and along with the provision of outdoor air, make this facility particularly attractive for the Large Building Study.

The only building site in which data collection has concluded to date is FCN. Data from LLC are being gathered and are not available for discussion. The current extent of the data analysis is limited to a qualitative discussion of carbon dioxide levels and a quantitative comparison of radon levels and building HVAC activity (see Figure 1), with radon correlated inversely to outdoor air levels.

The FCN building had initially exhibited radon levels of approximately 10 pCi/l, during U.S. Government Services Administration screening measurements, which are above the EPA recommended limit of 4 pCi/l. In early 1992, Radon Environmental Testing Corporation was requested to provide radon measurement and mitigation service to the building management. Passive sealing of slab cracks and penetrations was provided as well as increasing the level of OA by installing supply fans which now inject

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(\*) 1 ft<sup>3</sup>/m = 0.000472 m<sup>3</sup>/s. (\*\*) 1 ft<sup>2</sup> = 0.0929 m<sup>2</sup>.

OA to the AH. This reduced radon levels to below the 4 pCi/l limit and generally subjectively improved indoor air quality (IAQ). By intentionally reducing the OA intake, an increase in radon concentrations was exhibited to a peak level above 4 pCi/l throughout the building. Distinct average levels of radon can be identified from the data for a consistent level of OA intake. A clear comparison of radon levels versus outdoor air intake flow rate is evident in the Figure 1 of integrated EPERM data. The average radon level measured with no OA (2.98 pCi/l) was over twice that measured with an OA intake of 13.6 ft<sup>3</sup>/min/person (1.27 pCi/l). Continuous measurement data including IAQ data is not available at this time.

The LLC is a single story building fairly typical of some of the radon work already undertaken in other school buildings. It has an area of 18,000 ft<sup>2</sup> and has as its HVAC system an all-air system. Specifically it is a modified central station variable-air-volume (VAV) system. The system controls the indoor environment by utilizing VAV boxes; however, its configuration cannot allow it to be classified as a pure VAV system, although it is referred to as such.

Results of measurements at LLC indicate that radon reductions correlate with HVAC on time use. During week days, on time use of the HVAC system exhibits a lowering of radon concentrations, with the highest concentrations coinciding with the HVAC system turning on in the morning. Radon concentrations consistently decrease during the day, and the lowest concentrations of radon are recorded at the time of system shutdown. Figure 2 displays an example of a graph of daily radon concentrations peaking near 30 pCi/l versus the OA (16.6 ft<sup>3</sup>/min/person) rate of flow (as a step function) for LLC having 150 occupants. During the 12 hours of HVAC system inactivity, radon concentrations steadily increase to the high point (5 to 6 AM). The rate of decrease in radon concentrations is dependent on the rate of OA intake, with greatest reductions rates correlated to greater rates of OA intake.

## DISCUSSION

In both buildings radon results show an inverse correlation between OA intake levels and radon concentrations. This relationship is visible at every stage of air intake, indicating the greater the level of OA intake the less concentrations of radon result. The LLC exhibited the highest radon levels at the time when the AH turned on. A decrease in radon was consistent during the AH on time, and the lowest concentrations were measured at the time of AH shutdown (see Figure 2).

Tracer gas measurements indicate that zonal mixing, infiltration and overall pressure were dominated by HVAC control. Thermostat controls were placed on continuous fan operation. However, each of the 23 thermostat control boxes has unrestricted access and many were often found to be reset to cycle the AHs on/off for temperature control. This could create zones with active AHs which dominate adjacent areas. Unitary HVAC systems (such as FCN) present unique subjects for investigation.

## RESEARCH CONCLUSIONS

The FCN building showed a decrease in radon concentrations with increasing amounts of OA. The LLC exhibited a daily lowering of radon concentrations with increasing OA levels. Both buildings are being evaluated and field measurements are continuing on LLC.

The size and relative simplicity of the LLC made it a perfect candidate to begin development of the HVAC system diagnostic procedures. Particularly with regard to the familiar central station HVAC system. Evaluating the system, understanding the design intent, reestablishing air balance, and providing pressure can be controlled with this building and system.

Large buildings are not easily characterized since they are composed of many complex systems. The two buildings selected represent a start at increasing our understanding of these complex systems, and attempting to further current knowledge. Evaluation of the research results continues by use of the Florida Solar Energy Center Large Building Computer Model. Complete study findings are expected to be available by July 1993.

This research project was partly funded by the State of Florida, Department of Community Affairs.

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Number	Location Description	Baseline			
		Existing 06/06/92 06/16/92	13.8 cfm 06/16/92 07/01/92	0 cfm 07/03/92 07/06/92	5.5 cfm 07/08/92 07/13/92
1	1ST RECEPTION	2.22	1.51	3.28	2.24
2	TOM SCOTT'S OFFICE	1.91	1.81	3.67	2.40
3	JOE SCOTT'S OFFICE	1.61	1.77	4.07	2.72
4	TOM ANDERSON'S OFFICE	1.44	1.47	3.05	2.08
5	JOANN'S BIG OFFICE	1.16	1.43	2.65	1.67
6	JOANN'S 2ND OFFICE	1.28	1.42	2.75	1.93
7	KAREN'S OFFICE	1.20	1.36	2.50	1.50
8	FRONT RECEPTION AREA	1.22	1.25		
9	1ST LOBBY	1.24	1.29	2.17	1.56
10	RM 101	0.74	0.96		1.40
11	CID WEST	0.60	1.00		1.44
12	CID EAST	0.60	1.03		1.51
13	RM 200 SOUTH	1.39	1.27		1.87
14	RM 200 NORTH	1.40	1.30		1.86
15	RM 200 WEST	1.49	1.46		2.51
16	RM 201 EAST	1.39	1.36		2.44
17	RM 201 COMPUTER	1.50	1.42		2.42
18	RM 300 SOUTH	0.97	0.75	3.16	
19	RM 300 NORTH	0.85	0.83	3.14	
20	RM 301 WEST	2.81	1.22	2.87	1.92
21	RM 301 EAST	1.14	0.88	2.49	1.68
22	RM 301 COMPUTER	1.29	1.01	2.65	1.83
23	ELEVATOR	1.11	1.16		1.47
24	WAREHOUSE	0.61			0.82
25	ANITA'S OFFICE		1.26	3.36	1.99
26	MAINTENANCE OFFICE		1.41	2.81	1.95
27	JIM SCOTT'S OFFICE		1.47	2.91	2.00
Average Radon Level		1.32	1.27	2.98	1.90
High Reading		2.81	1.81	4.07	2.72
Low Reading		0.61	0.63	2.17	0.82

FIGURE 1. FINANCIAL CENTER BUILDING, AVERAGE RADON CONCENTRATION

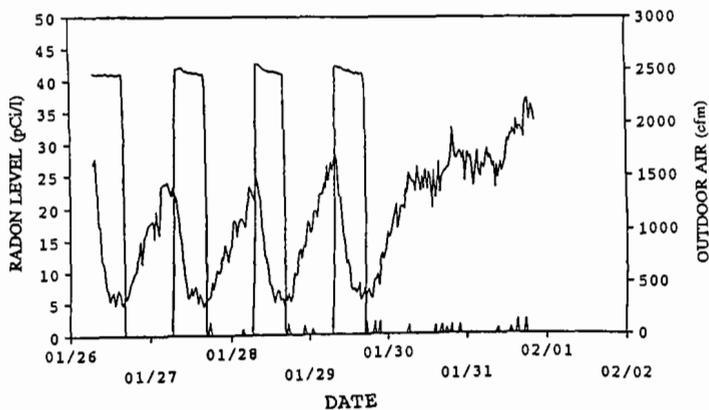


FIGURE 2. LIFE AND LEARNING CENTER, RADON CONCENTRATION

An Analytical Solution to Describe the Pressure/Flow  
Relationship in EPA's Soil-gas Chamber

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ABSTRACT

In order to better understand the production and transport of radon and other potential indoor air pollutants such as pesticides, bacteria, and landfill gases in soil, EPA has constructed a 16 m<sup>3</sup> soil-filled chamber instrumented to measure such parameters as pressure differences, air flow rates, and contaminant concentrations. An analytical model has been developed to describe the relationship between pressure differential and flow rate. This paper applies the classic *method of images* to simulate the boundary conditions imposed by the finite dimensions of the chamber. The resulting influence on constant pressure contours and the streamlines are shown.

INTRODUCTION

A number of indoor air pollutants, including pesticides, bacteria, landfill gases, and radon, originate in the soil surrounding a building. In order to better understand the processes by which these pollutants enter the building as well as the most appropriate methods for preventing their entry, a study of the transport mechanisms in soil was initiated. Numerous efforts to correlate measured indoor radon levels with radon values measured in the surrounding soil led to the conclusion that better experimental control of the parameters that influence the rate of radon entry would be required in order to develop and test models to predict indoor radon levels. Experimental control of these parameters is best accomplished in a laboratory environment. Consequently, a soil-gas chamber for studying radon movement in soil was designed.

While it has been widely purported (1-8) that pressure driven flow is the primary process by which radon and other soil-gas borne pollutants enter buildings, it is becoming more apparent (9-10) that diffusion may make an important contribution to indoor radon when the resulting indoor levels are in the modest range (less than 200 Bq m<sup>-3</sup>). While the diffusive mechanisms would be expected to differ somewhat for the different pollutants, the advective processes would affect most of the pollutants in a similar manner. This paper will concentrate on the advective transport processes, specifically on the pressure/flow relationships.

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.

A previous analytical model was developed (11) to describe the flow of soil gas into a cylindrical tube buried in the soil. Flow into this tube can be representative of either flow of soil gas into a drain tile surrounding the foundation of a building or flow directly through a perimeter crack between the floor slab and the wall. In reference (11), an analytical solution was developed for an infinitely long porous tube buried in the soil parallel to an infinite plane (the surface of the soil).

#### DEVELOPMENT OF THE EQUATIONS

Due to the practical limit on its dimensions, the laboratory chamber, designed to study soil transport characteristics, can not adequately simulate the infinite dimensions assumed by the analytical solution. The laboratory chamber is 2 m in height and 2 m x 4 m in area. The details of this chamber are described elsewhere (12, 13). In order to modify the analytical solution to match the boundary conditions of the finite box of soil, the classic *method of images* is employed. The method works because the linearity of Laplace's equation allows superposition of several solutions that can cooperatively satisfy the appropriate boundary conditions. The solutions that are applicable arise from a series of virtual images of the original solution whose origins lie outside the domain of interest. The method is very much analogous to using images of point electrical charges to simulate the interaction between a point charge and a grounded conducting surface such as a plane.

The equations governing transport under steady state conditions can be written in the form:

$$\nabla^2 P = 0, \quad (1)$$

$$\vec{v} = -\frac{k}{\mu} \nabla P, \quad (2)$$

$$D_0 \nabla^2 C - \frac{1}{\epsilon} \vec{v} \cdot \nabla C + G - \lambda C = 0, \quad (3)$$

where  $\nabla$  is the gradient operator,  $P$  is the pressure difference responsible for the flow,  $\vec{v}$  is the superficial velocity,  $k$  is the permeability of the soil to air movement,  $\mu$  is the dynamic viscosity of the soil gas,  $D_0$  is the effective diffusion coefficient of radon in the soil,  $C$  is the activity concentration of radon,  $\epsilon$  is the porosity of the soil,  $G$  is the generation rate of radon activity, and  $\lambda$  is the radon decay constant. For simplicity in solving these equations, the soil properties of permeability, porosity, and generation rate are taken to be uniform and isotropic.

Since the pressures differences involved are a thousand times smaller than atmospheric pressure, the flow will be considered incompressible. Equation (1) can be solved to yield the pressure distribution within the soil. Equation (2) then yields the velocity distribution throughout the soil. Solution of equation (3) provides the

concentration of radon at any location within the soil. Equation (3) is provided here primarily for completeness. Its solution will not be discussed in this paper.

The solution of equation (1) developed in reference (11) can be represented by

$$P(x, y) = P_c \ln \left( \frac{x^2 + (y + \sqrt{h^2 - b^2})^2}{x^2 + (y - \sqrt{h^2 - b^2})^2} \right) / \ln \left( \frac{h + \sqrt{h^2 - b^2}}{h - \sqrt{h^2 - b^2}} \right) \quad (4)$$

where  $P_c$  is the pressure in the cylinder,  $h$  is the depth of the cylinder below the surface of the soil, and  $b$  is the radius of the cylinder. When air flow is restricted to entering only through the finite area of soil surface defined by the impenetrable walls of a chamber, the solution becomes

$$\begin{aligned} P(x, y) = & P' \ln \left( \frac{x^2 + (y + \sqrt{h^2 - b^2})^2}{x^2 + (y - \sqrt{h^2 - b^2})^2} \right) \\ & + P' \sum_{i=1}^{\infty} \ln \left( \frac{(4hi + x)^2 + (y + \sqrt{h^2 - b^2})^2}{(4hi + x)^2 + (y - \sqrt{h^2 - b^2})^2} \right) \\ & + P' \sum_{i=1}^{\infty} \ln \left( \frac{(4hi - x)^2 + (y + \sqrt{h^2 - b^2})^2}{(4hi - x)^2 + (y - \sqrt{h^2 - b^2})^2} \right) \end{aligned} \quad (5)$$

where

$$P' = P_c \left[ \ln \left( \frac{h + \sqrt{h^2 - b^2}}{h - \sqrt{h^2 - b^2}} \right) + 2 \sum_{j=1}^{\infty} \frac{(-1)^{j+1}}{j 2^{2j}} \zeta(2j) \right]^{-1}, \quad (6)$$

$\zeta(2j)$  being the Riemann zeta function. For the laboratory apparatus,  $P' \approx 0.9 P_c$ . The two infinite series in equation (5) arise because an infinite number of images are required on each side of the chamber in order to provide the required symmetry to satisfy the boundary condition that no flow penetrates the chamber walls. Since this nearly incompressible flow has been treated as potential flow, the stream function can be expressed as

$$\begin{aligned} \psi(x, y) = & 2P' \left[ \tan^{-1} \left( \frac{y + \sqrt{h^2 - b^2}}{x} \right) - \tan^{-1} \left( \frac{y - \sqrt{h^2 - b^2}}{x} \right) \right] \\ & + 2P' \sum_{i=1}^{\infty} \left[ \tan^{-1} \left( \frac{y + \sqrt{h^2 - b^2}}{4hi + x} \right) - \tan^{-1} \left( \frac{y - \sqrt{h^2 - b^2}}{4hi + x} \right) \right] \\ & - 2P' \sum_{i=1}^{\infty} \left[ \tan^{-1} \left( \frac{y + \sqrt{h^2 - b^2}}{4hi - x} \right) - \tan^{-1} \left( \frac{y - \sqrt{h^2 - b^2}}{4hi - x} \right) \right] \end{aligned} \quad (7)$$

where  $\psi$  [ $\psi(x, y)$ ] is the stream function. The  $x$  and  $y$  components of velocity may be obtained by differentiating either equation (6) or (7)

$$v_x(x, y) = \frac{8kP'\sqrt{h^2-b^2}}{\mu} \left( \frac{xy}{[x^2+(y+\sqrt{h^2-b^2})^2][x^2+(y-\sqrt{h^2-b^2})^2]} + \sum_{i=1}^{\infty} \frac{(4hi+x)y}{[(4hi+x)^2+(y+\sqrt{h^2-b^2})^2][(4hi+x)^2+(y-\sqrt{h^2-b^2})^2]} - \sum_{i=1}^{\infty} \frac{(4hi-x)y}{[(4hi-x)^2+(y+\sqrt{h^2-b^2})^2][(4hi-x)^2+(y-\sqrt{h^2-b^2})^2]} \right) \quad (8)$$

and

$$v_y(x, y) = \frac{-4kP'\sqrt{h^2-b^2}}{\mu} \left( \frac{x^2+h^2-b^2-y^2}{[x^2+(y+\sqrt{h^2-b^2})^2][x^2+(y-\sqrt{h^2-b^2})^2]} + \sum_{i=1}^{\infty} \frac{(4hi+x)^2+h^2-b^2-y^2}{[(4hi+x)^2+(y+\sqrt{h^2-b^2})^2][(4hi+x)^2+(y-\sqrt{h^2-b^2})^2]} + \sum_{i=1}^{\infty} \frac{(4hi-x)^2+h^2-b^2-y^2}{[(4hi-x)^2+(y+\sqrt{h^2-b^2})^2][(4hi-x)^2+(y-\sqrt{h^2-b^2})^2]} \right) \quad (9)$$

Note that the infinite sums are also reflected in both the stream function and the velocity expressions. Equation (9) can be integrated over the surface of the soil where  $y = 0$  to yield the total flow rate through the system

$$Q = \frac{4\pi LkP'}{\mu} \quad (10)$$

By measuring  $Q$  and  $P_0$ , this equation and equation (6) provide an easy method of measuring the bulk permeability of the soil in the laboratory chamber.

#### DISCUSSION AND CONCLUSIONS

Figure 1 shows constant pressure contours for the central vertical plane along the length of the soil chamber. The cylinder is located at the center of the vertical  $y$ -axis. In the absence of the boundaries formed by the sides of the chamber, the constant pressure curves were circles centered on the vertical axis (11). Note the considerable deviation from circles induced by the finite dimensions of the chamber. This effect occurs because the boundary conditions require that no horizontal flow results at the impermeable surfaces. Figure 2 illustrates the streamlines. Streamlines which previously extended toward infinity in circular arcs now flow vertically near the sides of the chamber (indicating that the boundary conditions are satisfied). Despite the very considerable modifications in the isobars and the streamlines, however, the total flow rate is diminished by about only 10% from its value in an infinite block of uniform soil. In both Figures (1) and (2), only half of the chamber is shown. To the extent that the soil is uniform and isotropic, the flow pattern is completely symmetrical about the vertical  $y$ -axis. The other half of the chamber to the left would be represented by the mirror image of the curves shown.

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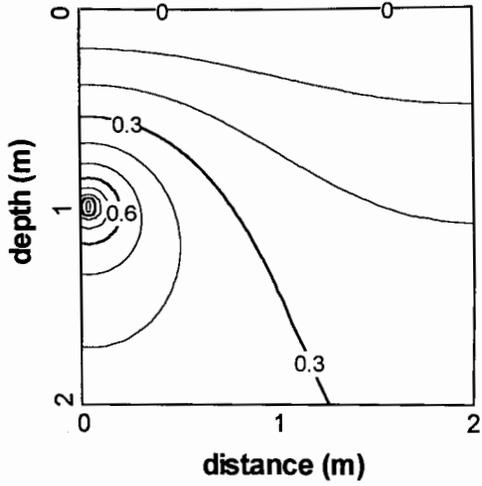


Figure 1. Calculated pressure contours

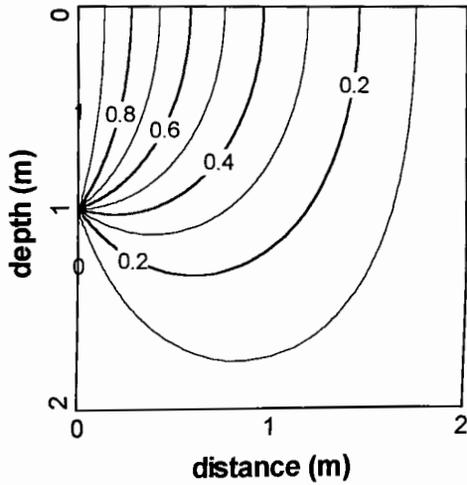


Figure 2. Calculated streamlines

*Session 2*

*Air Pollution*

*Dispersion Modeling*

## Uncertainties Of Using Short-Term Air Quality Concentrations To Estimate Annual Average Concentrations

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### ABSTRACT

EPA "Guideline" modeling procedures<sup>1</sup> allow the use of multiplying factors to convert 1-hour maximum concentration estimates to averaging times of 3, 8 and 24 hours. These factors as well as a factor to convert annual averages<sup>2</sup> are intended for inclusion into the T-SCREEN model<sup>3</sup>. In an effort to better understand the uncertainties in these conversions and in concentrations estimations using non-representative meteorological data, the Air/Superfund program funded a sensitivity study<sup>4</sup> to determine the range of effect that meteorological data might have on model estimations of 1-hour, 3-hour, 8-hour, 24-hour and annual average concentrations. Superfund type area and point sources were modeled using the Industrial Source Complex Short Term (ISC2) model with input from twenty seven widely spread National Weather Service (NWS) stations.

This paper presents the findings of the study as they relate to air stripping of contaminated water. SCREEN<sup>5</sup> model 1-hour estimates and converted 3-hour, 8-hour, 24-hour, and annual average values are compared to the ISC2 model results.

Understanding the range of uncertainties of the estimated concentrations is necessary to insure proper interpretation of such estimates in decision making.

### INTRODUCTION

Because it is easier to estimate or monitor short term ambient air concentrations, short term average concentrations are often used to estimate long term average concentrations. The SCREEN model was developed to estimate maximum 1-hour concentrations as a function of source-receptor distance and meteorological variability. In order to estimate maximum concentrations with longer averaging times, conversion factors<sup>1-2</sup> were developed (see Table 1).

Table 1. One hour conversion factors.

<u>Averaging Time</u>	<u>Multiplying Factor</u>
3 hour	0.9 (+/-0.1)
8 "	0.7 (+/-0.1)
24 "	0.4 (+/-0.1)
1 year	0.08 (+/-0.2)

In order to have widespread applicability and a factor of safety, these factors must produce conservative estimates of the expected impacts. Ultraconservative screening Air Pathway Analyses (APAs) may lead to unnecessary in-dept APAs and are not adequate for decision making in the early phases of the Superfund process. Not knowing how conservative the SCREEN model estimations might be, the Air/Superfund Program decided to do meteorological sensitivity studies in order to obtain an estimation of the amount of conservatism in APAs based on screening methods.

#### STUDY APPROACH

Superfund type area and point sources were modeled using the Industrial Source Complex Short Term (ISC2) model with meteorological data from twenty-seven widely spread National Weather Service (NWS) stations.

Superfund sources are generally low level sources and impacts of interest are generally close to the source. All modeling for this study was performed with the ISC2 model for ground level receptors assuming flat terrain and using rural dispersion coefficients. This paper presents the sensitivity study findings as they relate to air stripping of contaminated water.

Tables 2 list the air stripper source input data which were used in the model.

Table 2. Model inputs for the air stripper.

stack height	= 10 m	stripper height.	9 m
stack diameter	= 0.62 m	stripper diameter	3.6 m
stack temperature	= 293 °K	emission rate	1 g/s
stack velocity	= 8 m/s		

Table 3 contains the ISC2 model output from the Denver NWS meteorological data set for the air stripper assuming an emission rate of 1 gram per second. The average annual impact in  $\mu\text{g}/\text{m}^3$  for any receptor can be calculated by multiplying the corresponding factor by the pollutant emission rate in grams per second. For example, the ambient concentration resulting from an emission rate of 0.2 g/s at the receptor with polar coordinates of  $10^\circ$  and 50 meters is  $0.5 \mu\text{g}/\text{m}^3$  ( $2.5 \times 0.2$ ).

Maximum concentration factors for each receptor distance, disregarding receptor direction, are listed at the bottom of the table. These values are typically the values that screening methods attempt to estimate.

Table 4 contains the maximum annual impact value from each of the twenty seven meteorological data sets in descending order of magnitude. The highest values are listed at the top of the table and the lowest are listed at the bottom of the table. SCREEN model estimates are listed at the bottom of the table. There is good agreement between the SCREEN estimates and the ISC highest maximum estimates (San Juan) for receptor distances between 100 to 200 meters. When compared to the ISC2 lowest maximum estimates (Atlantic city), the SCREEN estimates are higher by a

factor of 4 to 24.

The model data outputs for each of the other averaging times and each meteorological data set were searched for the highest maximum concentration factors and for the lowest maximum concentration factors.

Table 3. Model output from Denver NWS meteorological data in ug/m<sup>3</sup> per g/s emission rate.

azimuthal direction	distance from source in meters								
	50	100	150	200	300	400	500	750	1000
10	2.5	9.8	11.0	10.0	7.4	6.0	5.2	3.9	3.0
20	2.2	8.7	9.6	8.6	6.3	5.0	4.2	3.0	2.3
30	2.0	7.3	7.7	6.7	4.7	3.6	2.9	2.0	1.5
40	1.6	5.3	5.5	4.7	3.3	2.5	2.0	1.3	0.9
50	1.2	3.9	4.0	3.4	2.4	1.7	1.3	0.9	0.6
60	0.8	2.4	2.4	2.0	1.4	1.0	0.7	0.5	0.3
70	0.6	1.7	1.6	1.4	0.9	0.6	0.5	0.3	0.2
80	0.7	2.1	2.1	1.7	1.2	0.8	0.6	0.4	0.3
90	0.8	2.5	2.4	2.0	1.3	1.0	0.8	0.5	0.4
100	0.9	2.8	2.9	2.5	1.7	1.3	1.0	0.6	0.4
110	1.1	3.5	3.8	3.4	2.4	1.8	1.3	0.8	0.6
120	1.1	3.8	4.1	3.7	2.6	1.9	1.4	0.8	0.5
130	1.1	4.0	4.5	4.0	2.8	2.0	1.5	0.9	0.6
140	1.2	4.3	5.0	4.6	3.3	2.4	1.8	1.0	0.7
150	1.4	4.7	5.2	4.7	3.4	2.4	1.8	1.0	0.7
160	1.9	6.3	7.1	6.4	4.5	3.2	2.4	1.4	0.9
170	2.3	8.4	9.8	9.0	6.4	4.6	3.5	2.0	1.3
180	2.3	8.9	10.8	10.2	7.4	5.4	4.1	2.4	1.6
190	1.8	6.6	7.5	6.7	4.7	3.4	2.5	1.4	0.9
200	1.5	5.1	5.4	4.7	3.1	2.2	1.6	0.9	0.6
210	1.5	4.4	4.7	4.1	2.7	1.9	1.4	0.8	0.5
220	1.5	4.6	4.9	4.4	3.0	2.2	1.6	0.9	0.6
230	1.7	5.0	5.4	4.8	3.4	2.4	1.8	1.0	0.7
240	1.7	4.9	5.2	4.6	3.2	2.3	1.7	1.0	0.6
250	1.6	4.5	4.7	4.1	2.8	2.0	1.4	0.8	0.5
260	1.6	4.5	4.7	4.1	2.8	2.0	1.5	0.8	0.5
270	1.8	4.9	5.1	4.4	3.0	2.1	1.6	0.9	0.6
280	1.9	5.1	5.2	4.6	3.3	2.4	1.8	1.0	0.7
290	1.9	5.1	5.3	4.6	3.3	2.4	1.9	1.2	0.9
300	2.0	5.5	5.7	5.1	3.7	2.8	2.3	1.6	1.2
310	2.2	5.9	5.9	5.1	3.6	2.8	2.2	1.5	1.2
320	2.2	5.8	5.7	4.8	3.3	2.5	2.0	1.4	1.1
330	2.1	5.7	5.5	4.6	3.1	2.3	1.8	1.3	1.0
340	2.1	6.2	6.5	5.7	4.1	3.2	2.7	2.0	1.5
350	2.2	6.6	7.0	6.3	4.6	3.7	3.2	2.5	2.0
360	2.4	8.7	9.4	8.3	6.1	5.0	4.3	3.4	2.6
MAXIMUM	2.5	9.8	11.0	10.2	7.4	6.0	5.2	3.9	3.0

The highest values come from the meteorological set which represents poor atmospheric dispersion. The lowest values come from the meteorological set which represents good atmospheric dispersion. The

SCREEN model was run and the one hour concentration values were converted to longer concentration averaging times using the conversion factors. These values are shown in Table 5 and compared to the ISC2 results for the same concentration averaging times. The ratios of SCREEN to ISC2 concentrations are also shown in Table 5.

Table 4. Maximum annual concentration estimations for each meteorological data set in ug/m<sup>3</sup> per year per g/s emission rate.

meteorological data set	distance from source in meters								
	50	100	150	200	300	400	500	750	1000
San Juan	7	29	30	26	18	13	11	8	6
San Francisco	4	18	21	19	13	10	8	5	3
Casper	5	18	20	17	11	8	6	3	2
Salem	3	13	19	18	14	10	8	5	3
Wichita	3	16	19	18	13	10	8	5	3
Helena	3	14	18	17	13	9	7	4	3
Salt Lake C.	4	12	16	16	12	10	8	5	4
Phoenix	5	13	14	13	10	8	7	5	3
Harrisburg	3	13	14	13	9	6	5	3	2
Spokane	2	11	13	12	8	6	5	3	2
Knoxville	3	10	13	12	10	8	6	4	3
Hartford	2	9	13	13	10	8	6	4	3
Atlanta	3	11	12	11	8	6	5	3	2
La Guardia	3	11	12	11	7	5	4	2	1
Philadelphia	3	10	11	10	8	6	4	3	2
Denver	2	10	11	10	7	6	5	4	3
Houston	2	9	11	10	8	6	5	3	2
Baton Rouge	2	8	11	10	8	6	5	3	2
Chicago	2	9	10	9	7	5	4	2	2
Wilmington	2	9	10	9	6	5	4	3	2
Bismarck	2	9	10	9	6	4	3	2	1
Cleveland	2	8	10	10	9	7	6	4	3
Huntington	2	8	10	10	9	7	6	4	3
Raleigh	2	7	9	9	7	6	5	3	2
Birmingham	2	7	9	8	7	6	5	5	4
Charleston	2	7	9	9	7	5	4	3	2
Atlantic City	2	7	8	7	5	4	3	2	1
SCREEN	26	28	28	29	28	26	25	26	24

## RESULTS

Examination of the ratios for the 1-hour averaging time reveal that for the location with the poorest dispersion the SCREEN model results agree quite well with the ISC2 results except possibly for an underestimation of about 20% of the ISC2 result at the point (distance) of maximum impact. For the location with the best dispersion meteorology, the SCREEN model overestimated the ISC2 result at the 1000 meter distant receptor by about 70%.

Examination of the ratios for the 3-hour averaging time reveal that

for the location with the poorest dispersion, the SCREEN model results agree quite well with the ISC2 results. For the location with the best dispersion, the SCREEN model results overestimate the ISC2 model results by a factor of 1.4 to 4.0 depending on the receptor distance from the air stripper.

Table 5. Comparison of ISC2 results to SCREEN results in ug/m<sup>3</sup> per gram per second emission rate.

	-----distance from source in meters-----								
	50	100	150	200	300	400	500	750	1000
<u>maximum 1-HR estimations:</u>									
SCREEN	330	350	350	360	340	330	310	320	290
ISC2 highest maxs.	290	320	450	470	460	390	330	300	280
ISC2 lowest maxs.	270	270	310	270	250	210	190	190	170
SCREEN/ISC2 high	1.1	1.1	0.8	0.8	0.7	0.8	0.9	1.1	1.0
SCREEN/ISC2/low	1.2	1.3	1.1	1.3	1.4	1.6	1.6	1.7	1.7
<u>maximum 3-HR estimations:</u>									
SCREEN (0.9)	300	320	320	320	310	300	280	290	280
ISC2 highest maxs.	280	310	310	270	260	240	240	240	230
ISC2 lowest maxs.	150	230	210	190	170	130	110	80	70
SCREEN/ISC2 high	1.1	1.0	1.0	1.2	1.2	1.3	1.2	1.2	1.2
SCREEN/ISC2/low	2.0	1.4	1.5	1.7	1.8	2.3	2.5	3.6	4.0
<u>maximum 8-HR estimations:</u>									
SCREEN (0.7)	230	250	250	250	240	230	220	220	210
ISC2 highest maxs.	210	250	230	230	200	170	160	150	140
ISC2 lowest maxs.	43	84	77	69	50	42	32	30	24
SCREEN/ISC2 high	1.1	1.0	1.1	1.1	1.2	1.4	1.4	1.5	1.5
SCREEN/ISC2/low	5.3	3.0	3.2	3.6	4.8	5.5	6.9	7.3	8.8
<u>maximum 24-HR estimations:</u>									
SCREEN (0.4)	130	140	140	140	140	130	120	130	120
ISC2 highest maxs.	57	110	140	150	130	98	74	49	38
ISC2 lowest maxs.	30	70	77	70	51	40	32	19	15
SCREEN/ISC2 high	2.3	1.3	1.0	0.9	1.1	1.3	1.6	2.7	3.2
SCREEN/ISC2/low	4.3	2.0	1.8	2.0	2.7	3.3	3.8	6.8	8.0
<u>maximum 1-YR estimations:</u>									
SCREEN (0.08)	26	28	28	29	28	26	25	26	24
ISC2 highest maxs.	7	29	30	26	18	13	11	8	6
ISC2 lowest maxs.	2	7	8	7	5	4	3	2	1
SCREEN/ISC2 high	3.7	1.0	0.9	1.1	1.6	2.0	2.3	3.3	4.0
SCREEN/ISC2/low	13	4	4	4	6	7	8	13	24

Examination of the ratios for the 8-hour averaging time reveal that for the location with the poorest dispersion the SCREEN model results agree quite well with the ISC2 results for receptors near the point of maximum impact. For the location with the best dispersion, the SCREEN model results overestimate the ISC2 model results by a factor of 3.2 to

8.8 depending on the receptor distance from the air stripper.

Examination of the ratios for the 24-hour averaging time reveal that for the location with the poorest dispersion, the SCREEN model results agree quite well with the ISC2 results for receptors near the point of maximum impact. For the location with the best dispersion the SCREEN model results overestimate the ISC2 model results by a factor of 1.8 to 8.0 depending on the receptor distance from the air stripper.

Examination of the ratios for the annual averaging time reveal that for the location with the poorest dispersion the SCREEN model results agree quite well with the ISC2 results for receptors near the point of maximum impact. For the location with the best dispersion, the SCREEN model results overestimate the ISC2 model results by a factor of 3.5 to 24 depending on the receptor distance from the air stripper.

#### CONCLUSIONS

Data from this study substantiates that in cities with poor dispersion, the SCREEN model results agree well with the ISC2 model results at the point of maximum impact.

Data from the study reveals that in cities with good dispersion, the SCREEN model overestimates ISC2 model results by factors of approximately 1.1, 1.5, 3, 2, and 4 respectively for concentration averaging times of 1-hr, 3-hr, 8-hr, 24-hr, and 1-yr at the point of maximum impact.

Overestimation by the SCREEN model of the ISC2 model results increases with source-receptor distance and with concentration averaging time. When 1-yr averaging time concentrations are derived from 1-hr averaging time values, they may be high by as much as a factor of 24.

Less conservative estimation of air strippers maximum annual average impacts might be made using factors such as those in Table 4. Using the San Juan values should result in estimations which are not conservative beyond a factor of 4. Using the Salt Lake City values should give estimations within a factor of 2.

The results of this study are based upon modeling of a typical air stripper and may not be applicable to other types of emission sources.

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## **FURTHER<sup>1</sup> DEVELOPMENT OF EMPIRICAL FACTORS FOR ESTIMATING AIR TOXIC SOURCE IMPACTS**

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### **ABSTRACT**

Atmospheric dispersion modeling estimates air pollutant concentrations as a function of receptor location, source type, and meteorological data set. In the early planning stages of Superfund activities, specific information about receptor location, source type and meteorological data is usually not known. This study was performed to further develop a tool by which gross air quality impacts could be made for specific types of Superfund sources<sup>2</sup>. By modeling generic typical sources repetitively with widely spread meteorological data sets, empirical factors representing conservative estimates of maximum downwind concentrations were obtained. Empirical factors for five averaging times (1-hr, 3-hr, 8-hr, 24-hr, and annual) were developed from the results of normalized modeling of generic sources. Source impacts can be estimated for receptors at various distances by multiplying the emission rate by the appropriate dispersion factor for each source type/receptor distance combination. Area and point sources typical of Superfund sites were modeled using the ISCST2 Model and meteorological data from twenty-seven different locations within the United States. Empirical factors (dispersion coefficients) for predicting concentrations as a function of receptor distance were derived for an estimation of the maximum 1-hr, 3-hr, 8-hr, 24-hr, and annual averaging times at various receptor distances.

### **INTRODUCTION**

Dispersion modeling of nine Superfund-type sources was performed to calculate normalized (unit emissions) concentration estimates versus distance. This modeling was performed to supplement and extend former U.S. EPA calculations in "Hazardous Waste TSDF - Fugitive Particulate Matter Air Emissions Guidance Document"<sup>3</sup>. The TSDF modeling was performed using the ISCLT Model and only annual average concentrations were estimated. To extend the usability of this type of estimation tool, concentrations were generated for additional averaging times including 1-hr, 3-hr, 8-hr, and 24-hr. In this analysis the geometric mean concentration was calculated for the maximum concentrations at all sites. In addition, the standard geometric deviation was calculated for each set of maximum concentrations (i.e., at each downwind distance. This combination of statistics and the listing of the highest and the lowest concentrations are given in the report and can be used to estimate the potential conservatism in air quality results calculated from the empirical factors.

## **ANALYSIS OBJECTIVES**

The purpose of this work was to examine the sensitivity of the Industrial Source Complex (ISC) Model<sup>4</sup> predictions to location specific meteorological data and to develop empirical factors which will approximate ISC model results. An "empirical factor" in this analysis is a factor which when multiplied by an emission rate results in a conservative estimate of the ambient air concentration that would have been estimated by running a more detailed model. The empirical factors were developed from results of normalized modeling of generic point and area sources. These factors can be used to estimate Superfund type source impacts for receptors at various distances by multiplying the emission rate by the appropriate empirical factor. Maximum annual average concentrations are included because they are necessary for chronic risk assessment analyses and short-term estimates are included to assess acute impacts.

## **MODEL PROTOCOL**

### **Model Methodology**

The updated version of the short-term Industrial Source Complex Model (ISCST2) was selected for this analysis. The ISCST2 Model is similar to its earlier version from 1979 to 1991 but has been reprogrammed and has a new format for imputing data in batch mode using keywords to indicate specific data components. The ISCST2 Model includes all model options and algorithms of the former versions and was operational on a personal computer (486/33 with extended RAM memory). The steps taken to generate the curves of normalized concentration estimates versus downwind distance using ISCST2 were very specific and straightforward.

### **Select Sources**

Nine sources representing those potentially found at Superfund sites were selected for modeling. These included six area sources ranging in size from a small 1 m by 1 m area to a 500 m by 500 m area. Characterization of the area sources was selected to characterize similar Superfund-type areas of fugitive emissions ranging possibly from a short-term accidental spill or dumping operation over a small area to a site-wide fugitive emission due to an open lagoon, unpaved roads, or open trench air stripping. The other three sources were point sources related to the representation on air strippers and soil vapor extraction operations. Emissions from a medium size air stripper and two sizes of soil vapor extraction units were modeled. Structure downwash of effluent was considered by including the dimensions of the stripper or extraction units themselves. These structures are typically adjacent to the vent and are the most likely to cause downwash of effluent plumes. The dimensions of these structures were taken from representative sizes and shapes of air strippers<sup>5</sup> and SVE units<sup>6</sup>.

### **Meteorological Data**

Surface meteorological observations of wind speed, wind direction, temperature, opaque cloud cover and other surface National Weather Service (NWS) parameters were obtained for 27 surface sites for the analysis. The year of most recent data was used along with associated nearby mixing height data.

### **Receptor Locations**

In the ISCST2 Model analysis of each of the nine sources, a receptor grid was used which covered all downwind directions (every 10 degrees) at a number of downwind

distances (from six to nine depending on source). The downwind distances were selected to obtain both a maximum concentration and a profile of concentration versus distance downwind. Receptor distances for area sources were measured from the center of the area source.

## RESULTS

Table I contains the empirical factors which were derived from this work. The project report contains additional information which enables the user to understand the amount of potential conservatism which may be included in estimates made with these factors. Table II and Figure 1 are examples of the project report graphs which demonstrates the amount of conservatism which could be in estimates made using these empirical factors.

## CONCLUSIONS

The empirical factors can be used to make preliminary estimations of Superfund type source emission impacts. These determinations will be useful in the Superfund Process prior to the final design phase when more detailed information about the source becomes available. Estimations using these factors should be of particular value in the identification of principal contaminants of concern, in the design of toxic monitoring plans (determination of needed detection limits), in the selection of remediation alternatives (especially if the emission control cost might makes the technology less desirable, and in the design of remediation activities (level of operation). The project report contains information for each source/concentration averaging time as depicted in Table 2 and Figure 1. This information can be used to obtain an indication of the potential amount of conservatism in the estimates. This information will in-turn indicate the probability that more detailed information might be beneficial before decisions are made on the empirical factor concentration data.

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**Table I. Empirical Factors in ug/m<sup>3</sup> per mg/s emission rate**

**Small Soil Vapor Extraction Point Source (500 cfm):**

averaging	----- receptor distance in meters -----								
<u>time</u>	<u>50</u>	<u>100</u>	<u>150</u>	<u>200</u>	<u>300</u>	<u>400</u>	<u>500</u>	<u>750</u>	<u>1000</u>
1-hour	13	7.3	5.0	3.8	2.6	2.0	1.6	1.1	.85
3-hour	5.5	2.8	1.8	1.3	1.0	.80	.64	.42	.30
8-hour	3.4	1.6	1.0	.89	.70	.55	.44	.29	.20
24-hour	2.2	1.0	.58	.39	.29	.23	.18	.12	.081
annual	.41	.17	.10	.070	.043	.029	.021	.012	.008

**Medium Soil Vapor Extraction Point Source (3000 cfm):**

averaging	----- receptor distance in meters -----								
<u>time</u>	<u>50</u>	<u>100</u>	<u>150</u>	<u>200</u>	<u>300</u>	<u>400</u>	<u>500</u>	<u>750</u>	<u>1000</u>
1-hour	1.0	.98	.99	.84	.63	.53	.44	.30	.23
3-hour	.58	.59	.49	.44	.32	.25	.19	.13	.10
8-hour	.49	.45	.36	.31	.21	.16	.12	.080	.065
24-hour	.37	.32	.30	.26	.17	.12	.083	.044	.030
annual	.075	.066	.045	.032	.018	.012	.009	.006	.005

**Medium Air Stripper Point Source (5000 cfm):**

averaging	----- receptor distance in meters -----								
<u>time</u>	<u>50</u>	<u>100</u>	<u>150</u>	<u>200</u>	<u>300</u>	<u>400</u>	<u>500</u>	<u>750</u>	<u>1000</u>
1-hour	.29	.32	.45	.47	.46	.39	.32	.30	.28
3-hour	.28	.31	.31	.27	.26	.24	.24	.24	.22
8-hour	.21	.25	.23	.23	.20	.17	.16	.15	.14
24-hour	.057	.11	.14	.15	.13	.10	.074	.049	.038
annual	.007	.029	.030	.026	.018	.013	.011	.008	.006

**1 x 1 Meter Area Source:**

averaging	----- receptor distance in meters -----				
<u>time</u>	<u>5</u>	<u>10</u>	<u>20</u>	<u>40</u>	<u>100</u>
1-hour	3200	1400	510	160	33
3-hour	2500	960	330	100	21
8-hour	1600	690	230	70	14
24-hour	690	280	92	28	5.6
annual	120	35	10	2.9	.55

**50 x 50 Meter Area Source:**

averaging	----- receptor distance in meters -----								
<u>time</u>	<u>50</u>	<u>100</u>	<u>150</u>	<u>200</u>	<u>300</u>	<u>400</u>	<u>500</u>	<u>750</u>	<u>1000</u>
1-hour	9.1	6.8	6.3	5.8	4.8	3.9	3.3	2.3	1.8
3-hour	8.1	5.1	3.7	2.7	1.8	1.5	1.2	.86	.66
8-hour	6.8	3.4	2.4	1.8	1.2	.95	.80	.56	.43
24-hour	3.4	2.0	1.2	.77	.46	.36	.29	.20	.15
annual	1.1	.40	.21	.13	.068	.042	.029	.014	.009

**100 x 100 Meter Area Source:**

averaging ----- receptor distance in meters -----

<u>time</u>	<u>100</u>	<u>150</u>	<u>200</u>	<u>300</u>	<u>400</u>	<u>500</u>	<u>750</u>	<u>1000</u>
1-hour	3.4	3.4	3.4	3.2	2.9	2.7	2.1	1.7
3-hour	2.3	1.8	1.4	1.2	1.1	1.0	.79	.64
8-hour	1.9	1.2	.96	.74	.70	.64	.51	.41
24-hour	.95	.69	.56	.48	.45	.42	.34	.28
annual	.29	.17	.11	.061	.038	.027	.014	.009

**150 x 150 Meter Area Source:**

averaging ----- receptor distance in meters -----

<u>time</u>	<u>150</u>	<u>200</u>	<u>300</u>	<u>400</u>	<u>500</u>	<u>750</u>	<u>1000</u>	<u>1200</u>
1-hour	2.3	2.3	2.3	2.2	2.1	1.8	1.6	1.4
3-hour	1.1	.91	.85	.79	.78	.69	.59	.51
8-hour	.92	.68	.56	.49	.48	.43	.37	.33
24-hour	.38	.29	.24	.22	.20	.16	.13	.12
annual	.14	.094	.054	.036	.025	.013	.008	.006

**300 x 300 Meter Area Source:**

averaging ----- receptor distance in meters -----

<u>time</u>	<u>300</u>	<u>400</u>	<u>500</u>	<u>750</u>	<u>1000</u>	<u>1200</u>	<u>1500</u>	<u>2000</u>
1-hour	1.1	1.1	1.1	1.1	1.0	.99	.92	.80
3-hour	.43	.42	.42	.40	.39	.38	.35	.30
8-hour	.27	.25	.25	.24	.24	.23	.22	.29
24-hour	.13	.12	.11	.11	.10	.090	.080	.068
annual	.040	.027	.020	.012	.008	.006	.004	.003

**500 x 500 Meter Area Source:**(values are in ug/m<sup>3</sup> per g/s emission rate)

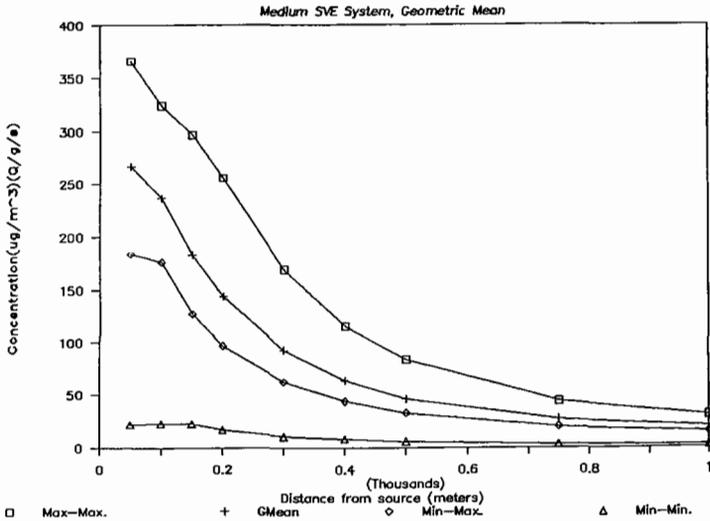
averaging ----- receptor distance in meters -----

<u>time</u>	<u>300</u>	<u>400</u>	<u>500</u>	<u>750</u>	<u>1000</u>	<u>1200</u>	<u>1500</u>	<u>2000</u>
1-hour	680	680	680	670	650	620	600	580
3-hour	250	250	250	240	240	230	230	220
8-hour	150	150	150	150	150	140	140	140
24-hour	89	86	85	84	82	79	75	69
annual	16	10	6.7	5.0	3.8	3.1	2.5	2.2

**Table II. Geometric mean, geometric standard deviation and extreme concentrations in ug/m<sup>3</sup> per gram/second emission rate averaged over all 27 sites for a medium soil vapor extraction system.**

	Receptor Distance (meters)									
	50	100	150	200	300	400	500	750	1000	
G-Mean	270	240	180	140	92	63	46	27	20	
G-STD	1.2	1.2	1.2	1.2	1.3	1.3	1.3	1.2	1.2	
n = 27 (total number of sites)										
Max-Max	370	320	300	260	170	120	83	44	30	
Min-Max	180	180	130	96	62	44	33	20	14	
Min-Min	22	23	23	17	10	8	6	3	2	
n = 972 (36 x 27 = total number of receptor locations)										

**Figure 1. Plot of 24-hour average concentration in ug/m<sup>3</sup> per mg/s emission rate as a function of downwind distance in meters for a medium soil vapor extraction unit.**



Max-Max curve represents the maximum anticipated concentration in the city with the poorest dispersion. GMean curve represents the maximum anticipated concentration in the city with median dispersion. MinMax curve represents the maximum anticipated concentration in the city with the best dispersion. MinMin curve represents the minimum anticipated concentration in the city with the best dispersion.

**Evaluating the Impact of Subsurface Contaminants  
On Indoor Air Quality Using Estimates  
From An Advective-Diffusive Transport Model**

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**ABSTRACT**

Subsurface contamination can affect indoor air quality and may adversely impact human health. Chemical vapors emanating from ground water and soil can enter a building through its foundation. The presence of pesticides and other toxic chemicals in indoor air has been found to cause risks to human health. The ability to accurately predict indoor air concentrations of air toxics attributable to subsurface contamination is, therefore, important in determining acceptable levels of residual soil and ground water concentrations beneath buildings.

This paper presents an exact solution to a one-dimensional transport equation for determining the mass flux of chemicals entering a building from the subsurface. The solution incorporates advection, diffusion and chemical phase equilibrium. In addition, the paper presents a screening-level procedure for predicting chemical concentrations in indoor air resulting from subsurface contamination beneath buildings. The screening-level methodology accounts for the advection and diffusion mechanisms governing chemical transport in subsurface media, as well as gas/liquid partitioning in soil. Calculations are presented to illustrate exact-solution and screening-level methodology comparisons.

## INTRODUCTION

Contaminants in the subsurface can infiltrate building substructures, accumulate in indoor air and adversely impact the health of building inhabitants. It is necessary to quantify the impact of these contaminants on indoor air quality, when performing human health risk assessments, establishing soil and ground water cleanup levels, and evaluating subsurface remediation alternatives associated with indoor exposure pathways. This paper presents an exact solution to a one-dimensional fate and transport equation for determining the mass flux of chemicals entering a building from the subsurface. In addition, the paper presents a simplified screening-level methodology for estimating the indoor air concentrations of these chemicals, as well as example calculations.

Much of the current literature addressing subsurface contaminant intrusion into indoor environments focuses on the transport of radon gas. Nazaroff et al.<sup>1,2</sup> investigate radon intrusion into buildings and identify pressure difference, radon generation rate, and soil permeability as the three most critical parameters for estimating the radon intrusion rate. Loureiro et al.<sup>3</sup> present a three-dimensional simulation of radon transport into houses and confirm the conclusion of Nazaroff et al.<sup>1,2</sup> For radon entry into houses, pressure-driven advection appears to be the controlling transport mechanism in highly permeable subsurface media. Phase equilibrium and adsorption onto soil particles are not expected to be significant for an inert radioactive gas.

In an attempt to address the inhalation risk associated with indoor air contaminants, methods used to estimate radon intrusion into indoor environments via advection have been used to estimate indoor air concentrations of volatile organic compounds (VOCs) emitted from subsurface media (Johnson and Ettinger<sup>4</sup> and Little et al.<sup>5</sup>). Unlike radon transport, however, VOC transport is influenced by phase equilibrium and adsorption onto soil particles. McCoy and Rolston,<sup>6</sup> for example, demonstrate that hydrophilic and sorptive characteristics tend to retard vapor transport via advection in unsaturated soil. Thus, using radon gas transport models to describe organic vapor transport may result in inaccurate indoor air concentration predictions.

This paper presents both refined and screening-level models for predicting the infiltration of chemical vapors into indoor environments. The refined model describes the mass flux of contaminant entering a building from the subsurface. This model is based on analytical solutions for subsurface vapor transport<sup>7,8,9,10</sup> incorporating phase equilibrium and adsorption phenomena. In the screening-level methodology, a nondimensional parameter (the modified Peclet number) is used to evaluate diffusive and advective transport mechanisms and determine which of these mechanisms governs contaminant transport. The modified Peclet number describes contaminant movement in terms of advection and diffusion time scales and vapor-liquid partitioning. Once the dominant transport mechanism is identified, indoor air concentrations are estimated using simplified transport equations. Example calculations are presented at the end of this paper to illustrate comparisons of the exact-solution and screening-level methodologies.

## SUBSURFACE CONTAMINANT TRANSPORT

The following sections present models for estimating the contaminant flux, the relative significance of advective and diffusive transport mechanisms, the indoor-outdoor pressure differential, and the indoor air concentration.

### The One Dimensional Fate and Transport Model

In a one-dimensional, homogeneous subsurface porous medium, the generalized mass conservation equation states that:

$$\frac{\partial C_T}{\partial t} + \frac{\partial J_s}{\partial x} + \lambda C_T = 0 \quad (1)$$

where:

- $C_T$  = total chemical concentrations per volume of soil, g/cm<sup>3</sup>;
- $\lambda$  = net degradation rate, day<sup>-1</sup>;
- $x$  = soil depth below the surface, cm;
- $J_s$  = chemical mass flux, g/cm<sup>2</sup>-s; and
- $t$  = time, s.

The chemical mass flux can be expressed as:

$$J_s = J_G + J_L = (-D_G \frac{\partial C_G}{\partial x} + vC_G) + (-D_L \frac{\partial C_L}{\partial x} + J_w C_L) \quad (2)$$

where:

$$D_G = \left( \frac{\theta_s^{10/3}}{\theta^2} \right) D_{ad}; \quad (3)$$

$$D_L = \left( \frac{\theta_a^{10/3}}{\theta^2} \right) D_{L_i}; \text{ and} \quad (4)$$

- $C_G$  = chemical concentration in soil gas, g/cm<sup>3</sup> air;  
 $C_L$  = chemical concentration in soil moisture, g/cm<sup>3</sup> water;  
 $J_G$  = mass flux in vapor form, g/cm<sup>2</sup>-s;  
 $J_L$  = mass flux in liquid form, g/cm<sup>2</sup>-s;  
 $J_e$  = chemical mass flux, g/cm<sup>2</sup>-s;  
 $J_w$  = liquid flux, g/cm<sup>2</sup>-s;  
 $D_G$  = effective air diffusion coefficient, cm<sup>2</sup>/s;  
 $D_L$  = effective water diffusion coefficient, cm<sup>2</sup>/s;  
 $D_a$  = air diffusivity, cm<sup>2</sup>/s;  
 $D_w$  = water diffusivity, cm<sup>2</sup>/s;  
 $\theta$  = total soil porosity,  $\theta = \theta_a + \theta_w$ , cm<sup>3</sup>/cm<sup>3</sup>;  
 $\theta_a$  = air-filled soil porosity, cm<sup>3</sup>/cm<sup>3</sup>;  
 $x$  = soil depth below the surface, cm; and  
 $v$  = vapor flow as described by Darcy's Law, cm/s.

The effective soil gas diffusion coefficient is equivalent to the air diffusivity multiplied by a tortuosity factor,  $\theta_a^{10/3}/\theta^2$ , to account for the reduced flow area and increase path length of diffusing gas molecules in soil. Soil air porosity may undergo substantial changes over time as soil dries out and when moisture is added by rainfall or by watering. In addition, the void space in soils may be unevenly distributed in multilayered soils. As a result, accurately accounting for soil porosity in an analytical model is practically impossible. The use of average values of soil porosity may be the most practical approach.<sup>11</sup>

By inserting Equation 2 into Equation 1 and assuming that:

- There is no steady water flux beneath the basement (i.e.,  $J_w = 0$ );
- There is no net degradation loss;
- Advection is driven by the indoor-outdoor pressure difference and the advection velocity is constant throughout the medium;
- The vapor flow is described by Darcy's Law as:

$$v = - \frac{k_v}{\mu} \frac{\partial P}{\partial x}; \text{ and} \quad (5)$$

- A three-phase equilibrium exists throughout the medium and the sorption equilibrium follows a linear isotherm;

Equation 1 can be written as:

$$R_G \frac{\partial C_G}{\partial t} - \frac{k_v}{\mu} \frac{\partial P}{\partial x} \frac{\partial C_G}{\partial x} = R_G \left( \frac{D_G}{R_G} + \frac{D_L}{R_L} \right) \frac{\partial^2 C_G}{\partial x^2} \quad (6)$$

where  $R_G$ ,  $R_L$  are the following partitioning coefficients:

$$R_G = \frac{\rho_v K_d}{H} + \frac{\theta_w}{H} + \theta_a, \quad (7)$$

$$R_L = \rho_w K_d + \theta_w + \theta_a H. \quad (8)$$

Additional parameters used in the above equations are defined below:

- $k_v$  = permeability of soil to soil gas, cm<sup>2</sup>;  
 $P$  = dynamic gas pressure, Pa (1 Pa = 10 g cm-s<sup>-2</sup>);  
 $\mu$  = dynamic viscosity of soil gas, g/cm-sec.  
 $R_G$  = vapor-phase partitioning coefficient, dimensionless;  
 $R_L$  = liquid-phase partitioning coefficient, dimensionless;

- $\rho$  = soil particle density, g/cm<sup>3</sup>;  
 $\rho_b$  = dry bulk density of soil,  $\rho_b = (1-\theta) \rho$ , g/cm<sup>3</sup>;  
 $\theta_m$  = moisture-filled soil porosity,  $\theta_m = w\rho_w$ , cm<sup>3</sup>/cm<sup>3</sup>;  
 $K_d$  = distribution coefficient, cm<sup>3</sup>/g; and  
 $H$  = Henry's law constant, dimensionless.

Since chemical vapor diffusion through soil occurs very slowly, it is assumed that subsurface chemical concentrations in soil gas ( $C_G$ ) and soil particles ( $C_{so}$ ) are in local equilibrium. Thus, the soil concentration can be related to the vapor-phase concentration, by assuming that  $K_d$  for individual contaminants in mixtures approaches that derived in a two-component system and that all contaminants dissolved in water act according to Henry's Law in multicomponent systems. Therefore,

$$C_G = \frac{H}{K_d} C_{so} \quad (9)$$

where:

- $C_{so}$  = concentration of chemicals in the soil, g/g;  
 $H$  = Henry's law constant, dimensionless;  
 $K_d$  = distribution coefficient, cm<sup>3</sup>/g; and  
 $C_G$  = concentration of chemicals in the soil pore spaces, g/cm<sup>3</sup>.

Using the above parameters, Equation 6 can be solved to estimate concentrations of chemicals in soil, and emission rates into air for any specific boundary condition.

The initial and boundary conditions used in the current assessment are the same as those used by Hwang et al.<sup>12</sup> where,

$$\begin{aligned}
 \text{Initial Concentration:} & \quad C_G = (H/K_d)C_{so} & @ t = 0, x > 0; \\
 \text{Boundary Condition 1:} & \quad C_G = (H/K_d)C_{so} & @ t > 0, x = \infty; \text{ and} \\
 \text{Boundary Condition 2:} & \quad C_G = 0 & @ t > 0, x = 0.
 \end{aligned}$$

The solution to Equation 6 using the stated conditions is (e.g., Jury et al.<sup>7</sup>):

$$C_G(x, t) = \frac{H}{K_d} C_{so} \left\{ 1 - \frac{1}{2} \operatorname{erfc} \left[ \frac{x + \frac{v_e t}{R_G}}{2\sqrt{D_{eff} t}} \right] - \frac{1}{2} \exp \left[ -\frac{v_e x}{R_G D_{eff}} \right] \operatorname{erfc} \left[ \frac{x - \frac{v_e t}{R_G}}{2\sqrt{D_{eff} t}} \right] \right\}, \quad (10)$$

where  $\operatorname{erfc}(n)$  is the complementary error function of the argument  $n$ ,  $v_e = -v = \frac{k_v}{\mu} \frac{\partial P}{\partial x}$ , and  $D_{eff} = \frac{D_G}{R_G} + \frac{D_L}{R_L}$ ; and all other parameters are as defined above.

Under the stated boundary conditions, Equation 10 can be used to estimate the instantaneous mass flux of chemical vapors infiltrating the basement,  $J_s(0; t)$ :

$$J_s(0; t) = \frac{-H/K_d C_{so} D_G}{\sqrt{\pi D_{eff} t}} \exp \left[ -\frac{(v_e t/R_G)^2}{4D_{eff} t} \right] - \frac{H/K_d C_{so} D_G v_e}{2 R_G D_{eff}} \left( 1 + \operatorname{erf} \left[ \frac{v_e t/R_G}{2\sqrt{D_{eff} t}} \right] \right), \quad (11)$$

where  $\operatorname{erf}(n)$  is the error function of the argument  $n$ .

### Indoor Air Concentrations

If a building ventilation rate is assumed, the flux calculated using Equation 11 can be used to estimate an indoor air concentration by applying the following relationship:

$$C_{indoor} = \frac{J_s A_{crack}}{Q}$$

where:

- $C_{indoor}$  = chemical concentration in indoor air, g/cm<sup>3</sup>  
 $J_s$  = chemical mass flux, g/cm<sup>2</sup>-s

$A_{crack}$  area of cracks in building foundation,  $cm^2$   
 $Q$  building ventilation rate,  $cm^3/s$ .

### The Modified Peclet Number

A dimensional analysis is necessary to determine the dominant mechanism of soil gas infiltration into buildings. Equation 6 can be nondimensionalized using the following nondimensional variables, commonly used when evaluating inert soil gas transport in subsurface media (Nazaroff and Sextro<sup>1</sup>; Johnson and Ettinger<sup>4</sup>):

$$C_{G^*} = C_G/C_r;$$

$$\frac{\partial}{\partial x_*} = L_D \frac{\partial}{\partial x};$$

$$P_* = \Delta P/P_r; \text{ and}$$

$$\tau_* = \tau(k_v \Delta P_r / L_p L_D \mu)$$

where  $C_r$ ,  $L_D$ ,  $L_p$ ,  $\Delta P$  are the characteristic concentration, diffusion length scale, advection length scale, and pressure difference, respectively. Equation 6 thus becomes:

$$R_G \frac{\partial C_{G^*}}{\partial x_*} - \frac{L_p}{L_D} \frac{\partial P_*}{\partial x_*} \frac{\partial C_{G^*}}{\partial x_*} = \frac{\mu L_p D_G (1 + \frac{R_G}{R_L} \frac{D_L}{D_G})}{k_v \Delta P_r L_D} \frac{\partial^2 C_{G^*}}{\partial x_*^2} \quad (12)$$

Ignoring the two characteristic length scales (diffusion and advection pathway lengths) introduced by Johnson and Ettinger<sup>4</sup>, the right-hand term of Equation 12 shows that the phase equilibrium characterizing subsurface contaminant transport has an impact on whether advection or diffusion controls the contaminant intrusion into the building. The partitioning-dependent Peclet number ( $Pe'$ ), is a modified version of the Peclet number introduced by Johnson and Ettinger<sup>4</sup>. The modified Peclet number accounts for liquid/vapor partitioning as shown below:

$$Pe' = \frac{k_v \Delta P_r L_D}{\mu L_p D_G \left( 1 + \frac{R_G}{R_L} \frac{D_L}{D_G} \right)} \quad (13)$$

Substituting Equations 3, 4, 7, and 8 into Equation 13, the modified Peclet number becomes

$$Pe' = \frac{k_v \Delta P_r L_D}{\mu L_p D_G \left( 1 + \frac{1}{H} \left( \frac{\theta_m}{\theta_a} \right)^{\frac{10}{3}} \frac{D_{L1}}{D_a} \right)} \quad (14)$$

$D_{L1}$  is, in general, four orders of magnitude less than  $D_{a1}$  and  $\theta_m$  is typically in the same order of magnitude as  $\theta_a$ . For an inert soil gas, such as radon, or many volatile organics which have high Henry's law constants, the Peclet number is insensitive to the chemical properties of contaminants. Soil gas transport is thus dominated by the pressure-difference-driven advection in subsurface material that is relatively permeable. However, for hydrophilic chemicals having low Henry's law constants, such as atrazine, bromacil, and 2,4 D, the advection mechanism is likely to be superseded by the combined vapor and liquid diffusion mechanism. Equation 11 indicates that chemical mass flux decreases with a decreasing Henry's law constant. The modified Peclet number (Equation 14), however, provides additional insight into the understanding of the subsurface contaminant transport. If the modified Peclet number is significantly less than 1, the diffusion mechanism governs chemical transport. If the modified Peclet number is greater than 1, the advection mechanism governs chemical transport.

### The Indoor Outdoor Pressure Differential

The  $\Delta P_r$  term in the above equations represents the pressure difference between indoor and outdoor environments. Wadden and Scheff<sup>3</sup> present a relationship to calculate the pressure differential due to wind and temperature effects using

the local annual average wind speed and temperature. This relationship has also been adopted by the American Society of Heating, Refrigerating, and Air-Conditioning Engineering<sup>14</sup> and is presented below:

$$\Delta P_r = \frac{P_v + \Delta P_c}{1 + \left(\frac{A_w}{A_L}\right)^{1/n}} \quad (15)$$

where:

- $\Delta P_r$  = pressure difference between indoors and outdoors, Pa;
- $P_v$  = static pressure over a building, Pa;
- $\Delta P_c$  = pressure difference due to a thermal gradient, Pa;
- $A_w$  = area of a building on the windward side, m<sup>2</sup>;
- $A_L$  = area of a building on the leeward side, m<sup>2</sup>; and
- $n$  = empirical exponent, 0.65 (Wadden and Scheff<sup>13</sup>).

The static pressure over a building can be described by:

$$P_v = 0.6008u^2 \quad (16)$$

where  $u$  is the wind velocity in m/s.

The pressure difference due to a thermal gradient is given by:

$$\Delta P_c = 0.0342Ph \left( \frac{1}{T_o} - \frac{1}{T_i} \right) \quad (17)$$

where:

- $P$  = atmospheric pressure, Pa;
- $h$  = distance from neutral pressure level to the point of interest, m;
- $T_o$  = outdoor temperature°, K; and
- $T_i$  = indoor temperature°, K.

### SCREENING-LEVEL METHODOLOGY

If project constraints do not allow for the solution of Equation 11, a screening-level methodology can be applied in order to obtain order-of-magnitude estimates of indoor air concentrations. The screening-level methodology involves the following procedure:

- Step 1: Estimate the modified Peclet number using Equation 14;
- Step 2: If the modified Peclet number is significantly less than 1, use Equation 20 (presented in the following section) to calculate the indoor/outdoor air concentration ratio due to diffusive mechanisms;
- Step 3: If the modified Peclet number is greater than 1, use Equation 21 (presented in the following section) to calculate the indoor/outdoor air concentration ratio due to advective mechanisms; and
- Step 4: Estimate the indoor air concentration.

### Indoor-Outdoor Pressure Differential

In order to carry out screening-level calculations, it is necessary to determine soil and chemical properties and estimate the indoor-outdoor pressure differential. Once this information is determined, the modified Peclet number can be calculated according to Equation 14.

### The Attenuation Coefficient

The modified Peclet number indicates the driving transport mechanism, and determines the appropriate attenuation coefficient for approximating indoor air concentrations. The attenuation coefficient ( $\alpha$ ) represents the ratio of air concentration indoors to the air concentration in soil pores ( $C_o$ ). Assuming the indoor air concentration ( $C_{indoor}$ ) remains constant under a steady building ventilation rate ( $Q_{mb}$ ) and a fixed crack space in the building substructure ( $A_{mb}$ ), the attenuation coefficient can be obtained from Equation 11,

$$\alpha = \frac{C_{indoor}}{C_G} = \frac{C_{indoor}}{\left(\frac{K_d}{H}\right) C_{\infty}} \quad (18)$$

$$\frac{A_{crack}}{Q_{vent}} \left\{ \frac{D_G}{\sqrt{\pi t D_{eff}}} \exp \left[ -\frac{(v_e t R_G)^2}{4 D_{eff} t} \right] + \frac{v_e D_G}{2 R_G D_{eff}} \left( 1 + \operatorname{erf} \left[ \frac{v_e t R_G}{2 \sqrt{D_{eff} t}} \right] \right) \right\} \quad (19)$$

where:

- t = time, s
- $A_{crack}$  = area of cracks in building foundation, cm<sup>2</sup>
- $Q_{vent}$  = building ventilation rate, cm<sup>3</sup>/s

If the soil gas transport is controlled by diffusion, Equation 19 becomes,

$$\alpha_d = \frac{A_{crack}}{Q_{vent}} \frac{D_G}{\sqrt{\pi t D_{eff}}} \quad (20)$$

where  $\alpha_d$  is the attenuation coefficient for diffusion-dominated transport scenarios, and all other parameters are defined above.

If the soil gas transport is controlled by advection, the attenuation coefficient can be obtained from a steady-state solution of Equation 19, also discussed by Little et al.<sup>5</sup> This coefficient is expressed as:

$$\alpha_a = \frac{A_{crack}}{Q_{vent}} \left( \frac{k_v}{\mu} \right) \left( \frac{\Delta P_r}{L_p} \right) \quad (21)$$

where  $\alpha_a$  is the attenuation coefficient for advection-dominated transport scenarios, and all other parameters are defined above.

#### Application

Equations 10 and 11 provide simple analytical solutions to the chemical vapor transport into the buildings. These solutions are conservative because they assume that the medium is uniformly contaminated. This conservativeness is appropriate where the level of contamination beneath a building foundation is poorly understood. Moreover, the medium is likely to be uniformly contaminated because the seasonal variation of the ground water table, whether the ground water is contaminated or not, ultimately provides a mixing mechanism in the subsurface medium. For a rapid assessment or screening analysis, the modified Peclet number can be used in conjunction with Equations 20 or 21 to estimate indoor air concentrations.

If ground water is the source of contamination and the vadose zone is considered relatively uncontaminated, Equation 6 can be used in conjunction with different initial and boundary conditions. Solutions to these conditions are available in the literature (e.g., Carslaw and Jaeger<sup>15</sup>, Crank<sup>16</sup>, van Genuchten and Alves<sup>17</sup>, Jury et al.<sup>7b</sup>). For a rapid assessment or screening analysis, the dominant mechanism from contaminant transport should be first determined by examining the modified Peclet number. Solutions to a simple steady-state diffusion equation for diffusion-controlled transport (see Crank<sup>16</sup> or Carslaw and Jaeger<sup>15</sup>) and Equation 17 for advection controlled transport can be used to yield reasonable estimates of indoor air concentrations.

#### EXAMPLE CALCULATIONS

Example screening-level calculations are carried out for soil contaminated with several chemicals including atrazine, benzene, bromacil, chloroform, dieldrin, lindane and 2,4 D. The medium is assumed to be a fine sand. Where possible, chemical and soil properties are cited from Johnson and Ettinger<sup>4</sup> and Jury et al.<sup>7</sup> to facilitate comparisons with literature values. Screening-level analysis procedures and results are discussed below.

#### Indoor-Outdoor Pressure Differential

Equations 15, 16 and 17 are used to determine the indoor-outdoor pressure differential. Table I presents assumptions made in applying Equations 15, 16 and 17, as well as pressure differential results. The pressure differential is estimated to be approximately 10 Pa, or 100 g/cm-s<sup>2</sup>. This differential reflects a 5.5 m/s wind speed and indoor and outdoor temperatures, of 75°F and 49°F, respectively. The h term in Equation 17 is assumed to have a value of 3 m. This value represents the distance from the neutral pressure level to the point of interest.

## Peclet Number

Table II presents some of the parameters in determining the modified Peclet number. The soil properties presented are for a fine sand. Table III summarizes Peclet number calculations as presented in Equations 3, 4, 7, 8 and 14. Table III also compares the modified Peclet number to the conventional Peclet number as presented in Johnson and Ettinger.<sup>4</sup> The conventional Peclet number presented in Johnson and Ettinger<sup>4</sup> does not account for phase equilibrium and adsorption. It is defined as:

$$P_e = \frac{k_v \Delta P_r L_D}{D_G \mu L_p}$$

The modified Peclet number,  $Pe'$ , is essentially equal to the conventional Peclet number for relatively hydrophobic chemicals such as benzene and chloroform.  $Pe'$  and  $Pe$  values for these chemicals indicate that advection governs contaminant transport. However, the modified Peclet number is notably less than the conventional Peclet number for hydrophilic chemicals.  $Pe'$ , for example, is between 60 and 2600 times less than  $Pe$  for atrazine, bromacil and 2,4 D. The modified Peclet number for these chemicals indicates that diffusion is the governing transport mechanism, whereas the conventional Peclet number incorrectly suggests that diffusion governs transport. The exact-solution attenuation coefficients discussed in the following section further illustrate the validity of the modified Peclet number.

## Attenuation Coefficients

Comparisons between screening-level and exact-solution attenuation coefficients reflect limitations associated with the screening-level methodology. Table IV presents Peclet numbers and attenuation coefficients for long-term (30-year) and short-term (1-year) emission scenarios. The attenuation coefficients in columns 4, 5, 7 and 8 are calculated using the screening-level methodology (Equations 20 and 21). Attenuation coefficients in columns 6 and 9 are calculated using based on the exact solution (Equation 19).

In cases where the modified Peclet number indicates diffusion-dominated transport ( $Pe' < 1$ ), the screening-level diffusion attenuation coefficients closely approximate the exact-solution attenuation coefficients for both long-term and short-term emission scenarios. Table IV shows that this is the case for atrazine, bromacil and 2,4 D. The agreement between exact-solution and diffusion-dominated screening level attenuation coefficients for these chemicals reflects the similarities between Equations 19 and 20. Equation 20 is obtained from Equation 19 by assuming a negligible indoor-outdoor pressure differential, and both equations reflect unsteady-state conditions.

It is interesting to note that the conventional Peclet numbers for atrazine, bromacil and 2,4 D incorrectly indicate that advection is the dominant transport mechanism and result in underestimates of attenuation coefficients (using Equation 21 instead of Equation 20) by factors ranging from 2 to 20. Equation 21 represents a steady-state vapor emission rate where (1) a constant indoor-outdoor pressure differential exists; (2) the vapor-phase contaminant concentration in soil pores remains constant; and (3) contaminant depletion via volatilization losses or partitioning in the subsurface medium does not occur. Equation 21 can be the ideal asymptotic solution of Equation 19 if the pressure differential remains large.

In cases where the modified Peclet number indicates advection-dominated transport ( $Pe' >> 1$ ), the screening-level advection attenuation coefficient, in general, agrees well with the exact-solution result. However, estimates obtained from the screening-level advection equation could underestimate short-term attenuation coefficients. Thus underestimation is due to the nature of unsteady-state emissions. For chemicals with strong absorption onto soil and moderate partitioning into water (e.g., dieldrin, lindane) the attenuation coefficient is governed by diffusion initially and by advection in the long term. As seen in Table IV, although advection is predicted to control lindane transport, unsteady-state diffusion actually controls the short-term emission and eventually advection becomes the governing mechanism.

## CONCLUSION

This paper reexamines the subsurface transport equation by incorporating phase equilibrium and chemical adsorption behavior, which is commonly considered in contaminant leaching and volatilization models. With a simple one-dimensional model, the indoor air concentrations can be estimated using the solution of an advective-dispersive transport equation. For a rapid assessment or screening analysis, the transport equation can be further simplified to an unsteady-state diffusion equation or a steady-state advection equation by evaluating the modified Peclet number. It is recommended that the modified Peclet number should be used instead of the conventional Peclet number.

Example calculations facilitate comparisons between the conventional and modified Peclet numbers, and the screening-level and exact-solution methodologies. Exact-solution results verify that the modified Peclet number more accurately reflects contaminant transport for hydrophilic organic chemicals such as atrazine, bromacil and 2,4 D. The use of the modified Peclet number and screening-level attenuation coefficients for relatively hydrophilic chemicals with high soil sorption coefficients requires further study.

Furthermore, this paper presents an analysis of one subsurface media and one set of boundary conditions. Studies that investigate variations in these parameters are necessary before the impact of subsurface contamination on indoor air quality can be more fully understood.

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**TABLE I**  
**Summary of Wind and Temperature-Induced Pressure**  
**Differential Calculations**

Parameter	Symbol	Value	Units
Wind Speed	v	5.5	m/s
Atmospheric Pressure	P	1.013 x 10 <sup>5</sup>	Pa
Distance from Neutral Pressure Level to Point of Interest	h	3	m
Outdoor Temperature	T <sub>o</sub>	282	K
Indoor Temperature	T <sub>i</sub>	297	K
Static Pressure over a Building	P <sub>v</sub>	18	Pa
Pressure Difference due to Thermal Gradient	ΔP <sub>t</sub>	1.9	Pa
Ratio of Building Side Areas	A <sub>w</sub> /A <sub>i</sub>	1.0	dimensionless
Empirical Exponent	n	0.65	--
Indoor/Outdoor Pressure Difference	ΔP <sub>r</sub>	10	Pa

**TABLE II**  
**Summary of Parameters Used in Modified Peclet Number and**  
**Attenuation Coefficient Calculations**

Parameter	Symbol	Value <sup>A</sup>	Units
Soil Permeability to Vapor	k <sub>v</sub>	10 x 10 <sup>-9</sup>	cm <sup>2</sup>
Indoor/Outdoor Pressure Difference	ΔP <sub>r</sub>	10 <sup>B</sup>	P <sub>a</sub>
Gas Viscosity	μ	1.8 x 10 <sup>-4</sup>	g/cm/s
Water-Filled Soil Porosity	θ <sub>w</sub>	0.12	dimensionless
Air-Filled Soil Porosity	θ <sub>a</sub>	0.26	dimensionless
Liquid Diffusivity	D <sub>Li</sub>	1 x 10 <sup>-5</sup>	cm <sup>2</sup> /s
Soil Dry Bulk Density	ρ <sub>v</sub>	1.7	g/cm <sup>3</sup>
Fraction Organic Carbon in Soil	F <sub>oc</sub>	0.002	dimensionless
Crack Area	A <sub>crack</sub>	1,000 <sup>C</sup>	cm <sup>2</sup>
Time Period	t	9.5 x 10 <sup>8</sup>	s
Ventilation Rate	Q	3.4 x 10 <sup>4</sup>	cm <sup>3</sup> /s
Characteristic Advection Length Scale	L <sub>p</sub>	1,000	cm

Notes:

<sup>A</sup> From Johnson and Ettinger<sup>4</sup> unless otherwise noted.

<sup>B</sup> Calculated as shown in Table I.

<sup>C</sup> Based on Wadden and Scheff.<sup>13</sup>

**TABLE III**  
Summary of Modified Peclet Number Calculations

Chemical	Henry's Law Constant (dimensionless) <sup>A</sup>	Distribution Coefficient K <sub>oc</sub> <sup>A</sup> (cm <sup>3</sup> /g)	Air Diffusivity D <sub>a</sub> <sup>B</sup> (cm <sup>2</sup> /s)	Liquid Diffusivity D <sub>l</sub> <sup>B</sup> (cm <sup>2</sup> /s)	Effective Air Diffusion Coefficient D <sub>a</sub> <sup>B</sup> (cm <sup>2</sup> /s)	Effective Liquid Diffusion Coefficient D <sub>l</sub> <sup>B</sup> (cm <sup>2</sup> /s)	Vapor Phase Partitioning Coefficient R <sub>G</sub> (dimensionless)	Liquid Phase Partitioning Coefficient R <sub>L</sub> (dimensionless)	Conventional Peclet Number (dimensionless)	Modified Peclet Number P' <sub>a</sub> (dimensionless)
Atrazine	2.5e-07	1.6e+02	5.0e-02 <sup>B</sup>	1.0e-05	3.9e-03	5.9e-08	2.7e+06	6.6e-01	1.4e+01	2.3e-01
Benzene	2.2e-01	8.3e+01	8.8e-02 <sup>C</sup>	1.0e-05	6.9e-03	5.9e-08	2.1e+00	4.6e-01	8.1e+00	8.1e+00
Bromacil	3.7e-08	7.2e+01	5.7e-02 <sup>B</sup>	1.0e-05	4.4e-03	5.9e-08	9.9e+06	3.6e-01	1.3e+01	3.4e-02
Chloroform	1.2e-01	2.9e+01	1.1e-01 <sup>D</sup>	1.0e-05	8.6e-03	5.9e-08	2.1e+00	2.5e-01	6.5e+00	6.5e+00
Dieldrin	6.7e-04	1.2e+04	4.4e-02 <sup>B</sup>	1.0e-05	3.4e-03	5.9e-08	6.1e+04	4.1e+01	1.6e+01	1.6e+01
Lindane	1.3e-04	1.3e+03	5.0e-02 <sup>B</sup>	1.0e-05	3.9e-03	5.9e-08	3.4e+04	4.5e+00	1.4e+01	1.3e+01
2,4 D	5.6e-09	2.5e+01	5.0e-02 <sup>B</sup>	1.0e-05	3.9e-03	5.9e-08	3.4e+07	1.9e-01	1.4e+01	5.2e-03

Notes:

A Jury<sup>10</sup>  
 B Estimated Value  
 C Johnson and Ettinger<sup>4</sup>  
 D USEPA<sup>20</sup>

**TABLE IV**  
Comparison of Screening-Level and Exact-Solution Attenuation Coefficients

	Conventional Peclet Number Pe (dimensionless)	Modified Peclet Number Pe' (dimensionless)	Screening-Level Unsteady-State Diffusion Attenuation Coefficient <sup>A</sup> @ T = 30 yrs (Equation 20) (dimensionless)	Screening-Level Steady-State Advection Attenuation Coefficient <sup>B</sup> @ T = 30 yrs (Equation 21) (dimensionless)	Exact Solution Unsteady-State Diffusion & Advection Attenuation Coefficient @ T = 30 yrs (Equation 19) (dimensionless)	Screening-Level Unsteady-State Diffusion Attenuation Coefficient @ T = 1 yr (Equation 20) (dimensionless)	Screening-Level Steady-State Advection Attenuation Coefficient @ T = 1 yr (Equation 21) (dimensionless)	Exact Solution Unsteady-State Diffusion & Advection Attenuation Coefficient @ T = 1 yrs (Equation 19) (dimensionless)
Atrazine	1.4e+01	2.3e-01	7.0e-06	1.6e-06	7.0e-06	3.8e-05	1.6e-06	3.8e-05
Benzene	8.1e+00	8.1e+00	6.5e-08	1.6e-06	1.6e-06	3.6e-07	1.6e-06	1.6e-06
Bromacil	1.3e+01	3.4e-02	5.9e-06	1.6e-06	5.9e-06	3.2e-05	1.6e-06	3.2e-05
Chloroform	6.5e+00	6.5e+00	7.3e-08	1.6e-06	1.6e-06	4.0e-07	1.6e-06	1.6e-06
Dieldrin	1.6e+01	1.6e+01	7.7e-06	1.6e-06	8.5e-06	4.2e-05	1.6e-06	4.3e-05
Lindane	1.4e+01	1.3e+01	5.9e-06	1.6e-06	6.7e-06	3.2e-05	1.6e-06	3.3e-05
2,4 D	1.4e+01	5.2e-03	3.7e-06	1.6e-06	3.7e-06	2.0e-05	1.6e-06	2.0e-05

Notes:

A Based on a crack area of 1000 cm<sup>2,13</sup>, a ventilation rate of 3.4 cm<sup>4</sup>/s and a time period of 30 years.  
 B Based on a crack area of 1000 cm<sup>2,13</sup>, a ventilation rate of 3.4 cm<sup>4</sup>/s and a characteristic advection length scale of 1000 cm.

**PRELIMINARY INVESTIGATION OF UNCOMBUSTED AUTO FUEL  
VAPOR DISPERSION WITHIN A RESIDENTIAL GARAGE MICROENVIRONMENT**

by

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**ABSTRACT**

Evaporative emissions from vehicles in an attached garage may represent a significant source of indoor pollution and human exposure. A pilot field study was undertaken to investigate potential in-house dispersion of evaporative emissions of uncombusted fuels from a vehicle parked inside an attached garage. In a set of experiments using sulfur hexafluoride (SF<sub>6</sub>) tracer gas, the multizonal mass balance model, CONTAM88, was used to predict interzonal air flow rates and SF<sub>6</sub> concentration distributions within the garage and house. Several experiments were included to evaluate the effect of meteorology and mechanical mixing mechanisms on the dispersion of automobile fuel vapor. Measurements indicated that approximately three percent of the garage maximum concentration was measured in a room adjacent to the garage. The model successfully predicted garage concentrations under well mixed conditions, but underpredicted the measured concentrations within various rooms of the house, in which mixing was incomplete. Multizonal mass balance models such as CONTAM88 may be useful in approximating contaminant concentrations at various locations within the house.

**INTRODUCTION**

The introduction of oxygenated auto fuels and fuel additives (alcohols and ethers) into the U.S. motor vehicle fleet has served to reduce tailpipe emissions of carbon monoxide and total hydrocarbons<sup>(1)</sup>. Tailpipe emissions represent an obvious source of *ecological* pollution, however evaporative emissions from vehicles in attached garages may represent an important source of indoor (i.e. *microenvironmental*) pollution.

In-house and attached garage concentration of evaporated (uncombusted) fuel species from an automobile's fuel system may represent a significant component of total human exposure to these chemicals. The use of alcohol and ether additives increases the fuel vapor pressure, and hence the evaporation rate<sup>(2)</sup>. The magnitude of in-house concentration of a chemical species depends upon the emission rate of evaporating fuel, the concentration of the component species within the liquid fuel, and the air flow rates between garage and house. Measurement of these critical variables enables the development of predictive models useful in population exposure assessment.

This study examines the potential for dispersion of evaporative emissions from an auto fuel system into a residence from an attached garage. A series of field experiments were conducted to obtain estimates of in-house ambient concentration of fuel vapor components resulting from normal automobile use scenarios. A single family house with attached garage was selected as the test site. Air flow rates between the garage and various zones within the house were measured using SF<sub>6</sub> tracer gas. A multizonal mass balance model was used to predict the spatial and temporal contaminant dispersion within the house. Previous investigation has shown that multizonal mass balance models may be useful in designing field study monitoring strategies<sup>(3)</sup>. Modeling results were compared to SF<sub>6</sub> measurements in order to investigate the possibility of using the model to predict methanol and/or other

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alternative fuel dispersion in the garage and throughout the house. Methanol emissions and concentration distributions were examined in a later phase of this pilot study. Analyses of methanol concentration and supporting modeling results will be presented in subsequent report.

## MATERIALS AND METHODS

### RESIDENCE DESCRIPTION

During the summer of 1992, a house in Raleigh, North Carolina was chosen to study in-house dispersion of evaporative emissions of uncombusted automobile fuels from a vehicle parked inside an attached garage. This study determined quantitative flow rates between the garage (pollutant source) and selected rooms of the house. The first story of this two story house consisted of the master bedroom, a bathroom, a den, the family room, the kitchen and the dining room (Fig. 1); the second story of the house includes three bedrooms and a bathroom. One second story bedroom was located directly above the garage. The total volume of the garage was 95 m<sup>3</sup>. The house physical characteristics were measured during the first day of the study. These measurements were subsequently used to model SF<sub>6</sub> concentration distribution in the garage and within the house. The SF<sub>6</sub> dispersion analysis was used to calculate interzonal air flows and to calculate contaminant concentrations in order to determine the rooms with significantly different concentrations.

### MASS BALANCE MODEL

The multizonal mass balance model used in this investigation is the National Institute of Standards and Technology (NIST) model, NBSAVIS/CONTAM88<sup>(6)</sup> developed for the Environmental Protection Agency to simulate transient contaminant concentration distribution in buildings. The model is based on the element assembly approach, which assumes that a building can be represented as a combination of well-mixed zones linked by flow and kinetic elements (contaminant mass transport and decay). CONTAM88 solves a set of mass balance and flow equations. The mathematical formulation of the contaminant concentration is:

$$[ W ] \vec{C} + [ M ] \frac{d\vec{C}}{dt} = \vec{G} \quad (1)$$

where:

- C = Vector containing the discrete concentration values
- [W] = System mass transport matrix which contains flow rate data
- [M] = System matrix which contains mass (volume) data
- G = System generation vector containing kinetics data.

NBSAVIS is a preprocessor to CONTAM88 which allows the idealization of a building through the generation of a file that describes the building configuration, including indoor and outdoor contaminant sources. Data input to NBSAVIS is facilitated by a series of data entry screens that allow the user to specify: interior and exterior wall types; interior and exterior doors, windows, open passageways; filters and fans; room descriptions; and heating, ventilation, and air conditioning (HVAC) system descriptions. NBSAVIS then calculates the interzonal air flow rates and system matrices. NBSAVIS was used to build an idealization of the house. The parameters that were measured in order to run NBSAVIS are:

- . The house physical dimensions (including all windows, doors and other openings).
- . The house HVAC system output as well as all the locations of the vents with air flow rates.
- . The contaminant source information (name, molecular weight, emission rate).
- . The location of the source (inside the garage).
- . The temperatures of the various rooms in the house.
- . The outdoor meteorological conditions (temperature, wind speed and wind direction).

## EXPERIMENTAL DESIGN

Three experiments in which SF<sub>6</sub> was released in the garage and traced inside the garage and the house were designed and implemented. SF<sub>6</sub> was chosen because it is non-toxic, stable with respect to chemical reactions; its removal due to deposition is negligible and it can be measured in very low concentrations with high accuracy<sup>(6)</sup>. A diluted mixture of SF<sub>6</sub> in nitrogen (0.362g SF<sub>6</sub> / m<sup>3</sup>) was prepared and used in all experiments. Samples were analyzed using gas chromatography/electron capture detection (GC/ECD), with a lower detection limit of 20 parts per trillion volume (ppt). Measurement accuracy was within 5%. Measurement precision (standard deviation) was within 5% of the measured concentration. During the entire study the outdoor temperature ranged between 19 C and 23 C, the wind speed did not exceed 0.5 m/s and the wind direction varied. The low wind speeds were mainly due to shielding of the house and property by trees.

The first experiment was designed to assess the percentage of contaminant that infiltrates in the house from the garage. A car was parked in the garage with the front of the car facing an interior wall of the garage. In this experiment five automated sequential syringe samplers<sup>(6)</sup> were used. Three samplers were placed in the house: one in the kitchen, one in the den and one in the bedroom above the garage. The remaining two samplers were located in the garage. One sampler was placed on the car roof, one was placed on the garage floor, next to the car. The garage door was closed during the experiment. SF<sub>6</sub> was released for 20 min at a rate of 1 liter per minute (l/min). The total mass of SF<sub>6</sub> released was 7.23 mg. The SF<sub>6</sub> source was located next to the gasoline tank on the passenger side of the car. A large box fan was used next to the source to create a well mixed condition. Samplers in the garage were started simultaneously with the SF<sub>6</sub> source. At the end of the SF<sub>6</sub> release (20 min), the three samplers inside the house were activated.

The second experiment was designed to investigate how quickly the concentration in the garage drops after the garage door is opened. In this experiment no car was in the garage. Air samples were taken at two vertical locations in the garage. The upper sample location was centered 2 feet from the garage ceiling while the lower sample location was centered 2 feet above the floor. The samples were analyzed in real time. SF<sub>6</sub> was released in the garage for 10 min at a rate of one l/min for a total mass released of 3.62 mg. The box fan was used to create a well mixed condition. At the end of the 10 min release time, the fan was turned off and the garage door was opened.

Experiment three was performed to test the well mixed garage assumption. Five syringe samplers were used in the garage, one on the car roof, one next to the driver's side, one next to the passenger side, one in front of the car (back wall location), and one in the back of the car (next to the garage door). No fan was used, and sampling time was set to 12 min intervals for all the samplers. SF<sub>6</sub> was released for 20 min at a rate of 1 l/min. The SF<sub>6</sub> source was located next to the gas tank on the passenger side of the car. The garage door was closed during the experiment.

## RESULTS AND DISCUSSIONS

During the first experiment, CONTAM88 was used to simulate the dispersion of SF<sub>6</sub> in the garage and throughout the house. Good agreement was found between simulated and measured data (Fig. 2). Differences may be due to a lack of complete mixing in the garage. There were two samplers in the garage; the one on the passenger side (labeled LEFTGARAGE in Fig. 2) showed a sharp drop of concentration approximately 30 min after the experiment started. This sampler was located close to the kitchen door, therefore the drop in concentration may be due to local air exchange. The other sampler (labeled TOPGARAGE in Fig. 2) agrees better with the model, which assumes a well mixed condition.

Modeling results consistently underpredicted the concentration in all the rooms in the house (Fig. 3). The highest concentration was measured and modeled in the kitchen; followed by the den and then the bedroom above the garage. Overall, the model predicted a behavior similar to the data. However, the model underpredicted the kitchen and bedroom concentrations by approximately 30%, and the den concentrations by approximately 10%. The model assumption of well mixed zones was not satisfied in the house because of the absence of forced mixing. The model predicted that the maximum concentration attained in the kitchen would be 2% of the maximum concentration in the garage, while measurements showed that the maximum relative concentration was approximately 3%.

Following the completion of SF<sub>6</sub> injection, the concentration in the garage began to decrease, while the

concentrations in the kitchen and the other rooms continued to rise. The time delay (phase lag) between the modeled maximum concentration in the garage and the kitchen was approximately 15 minutes; between the family room and the garage the time delay was approximately 30 minutes. In the bedroom the concentration was still rising 50 min after emission stopped (Fig. 3). The measured phase lag in concentrations between the various rooms of the house is also predicted by the model (Eq. 1). Conservation of mass ( $SF_6$ ) - within the context of a box model - requires that a loss of mass from one box (e.g. the garage) be accounted for in a net increase of mass in the other boxes (e.g. other rooms of the house; the outdoors).

In the second experiment, CONTAM88 was used to simulate contaminant build up and decay after the garage door was open. Modeling results were in agreement with the measurements (Fig. 4). After the garage door was opened the  $SF_6$  concentration decreased to less than 10% of the initial concentration in 3 minutes. Similar results were found using the decay from the modeling results. This decay rate corresponds to approximately 45 air changes per hour (ACH). During testing the wind speed was less than 0.2 m/s, therefore this high exchange rate is likely due to mechanical mixing that occurred when the garage door was opened. These results were supported by observations during smoke release experiments.

During the third experiment measurements were performed to test the well mixed box assumption. Model simulation was used to determine locations in the garage where the well mixed condition existed. Simulation results agreed with the data collected at the car roof, back of the garage, and the passenger side locations. The data collected near the garage door and driver side locations were approximately half of the model predictions. Total mixing occurred between 60 and 90 min after the  $SF_6$  release stopped (Fig. 5). These results show that sampler locations cannot be assumed to measure average (well mixed) concentrations, particularly during the period of contaminant emission. However, for constant sources, a steady state regime may develop in the garage and house, resulting in quasi-mixed conditions.

## CONCLUSIONS

Good agreement was found between modeling and experimental results in the garage when the well mixed assumption was verified (box fan on). In the rooms adjacent to the garage, the model underpredicted the concentration of  $SF_6$ . The model did help assess the broad trend of concentration distribution in those rooms. Approximately three percent of the maximum garage concentration was measured in the kitchen and 1.5 percent in the upstairs bedroom. These experiments were performed with the door between the kitchen and garage always closed. Higher in-house relative concentrations can be expected when this connecting door is opened.

When mixing was not forced (box fan off) within the garage, the well mixed assumption was not valid at locations next to the garage door and the kitchen door, but the other locations in the garage showed more thorough mixing. It took 60 to 90 min for total mixing to occur after the release of  $SF_6$  stopped. Furthermore, the well mixed assumption did not hold during the contaminant release time.

Preliminary results showed that multizonal mass balance models such as CONTAM88 may be used to approximate contaminant concentrations within various locations of the house provided sampling time and location are chosen judiciously. These models may help identify the locations where mixing occurs and the time duration to attain well mixed conditions. The models may help choose sampler locations and sampling time during a field study. Locations of expected high concentration gradients (near locations of local air exchange, such as doors and windows) must be sampled more intensively than locations of low concentration gradients (remote from locations of local air exchange). Furthermore, CONTAM88 can be used to successfully model the dispersion of uncombusted fuel vapor inside a residence and its attached garage. For pollutant emissions in an attached garage, sampling locations should be next to the garage door and any connecting (interior) doors and windows; one sampler in another location in the garage is sufficient (car roof or back of garage, etc). Sampling time will be dependent on the contaminant source release period and the time the source takes to reach steady state.

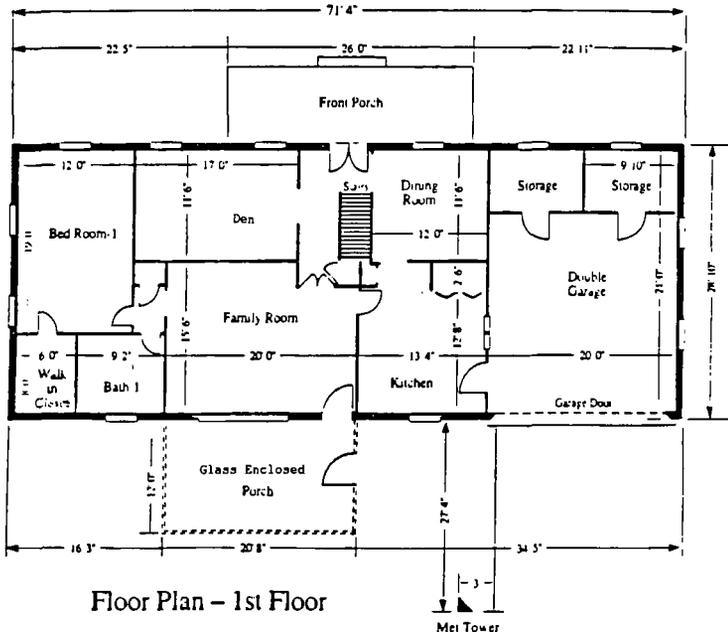
The potential exists for in-house exposure to emissions (uncombusted fuel vapors and exhaust) from a vehicle in an attached garage. Therefore, the introduction of alternative fuels and fuel components into the U.S. automobile fleet will result in residential exposure to these chemicals and their combustion by-products. An exposure assessment project is ongoing to quantify potential human exposures. The models evaluated here are being incorporated into this project.

## DISCLAIMER

This paper has been reviewed in accordance with the U.S EPA's peer review and administrative review policies and approved for presentation and publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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**Figure 1.** Residence floor plan. A second floor bedroom (not shown) was located directly above the garage.

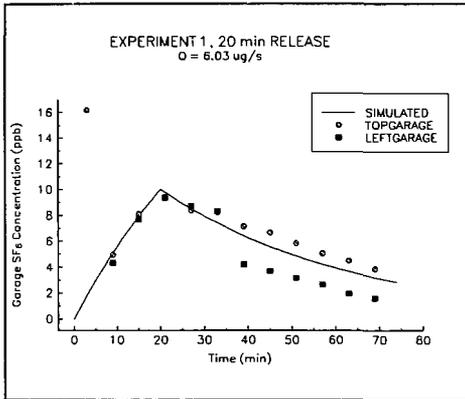


Figure 2. Simulated and measured garage transient concentrations during and after a 20 min SF<sub>6</sub> emission.

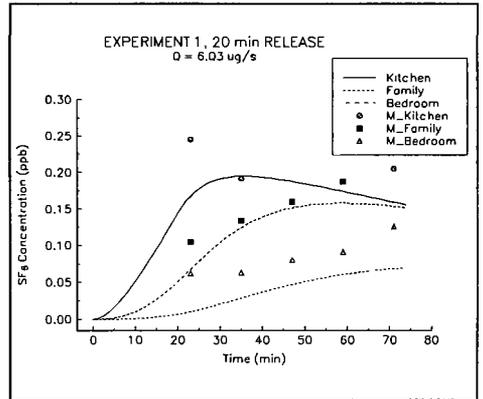


Figure 3. Simulated and measured (M) transient in-house concentrations during and after a 20 min SF<sub>6</sub> emission.

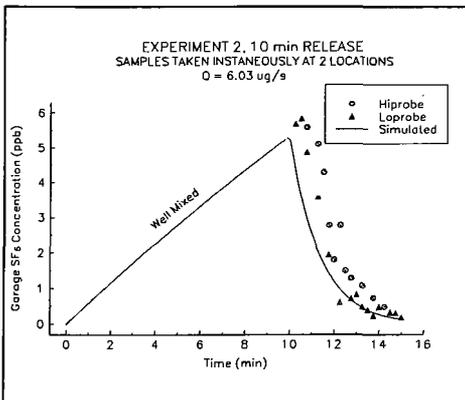


Figure 4. Simulated and measured SF<sub>6</sub> decay after 10 min SF<sub>6</sub> emission and after the garage door is opened.

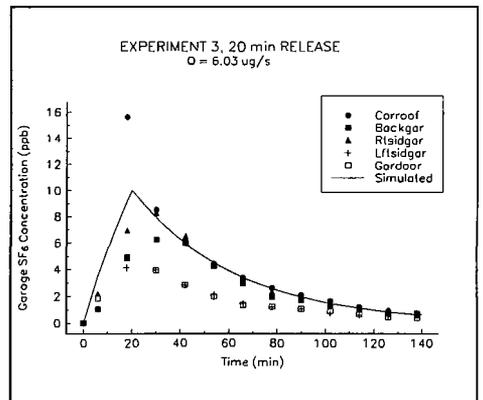


Figure 5. Simulated (well mixed) and measured transient concentrations at various locations in the garage.

## Modelling Ozone Deposition Onto Indoor Surfaces

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### ABSTRACT

Modelling the deposition of pollutants onto surfaces often requires the inclusion of two separate factors: the transport and surface uptake resistances. In this paper, the surface uptake resistance for ozone onto several common indoor surfaces was examined by measuring the mass accommodation (or "sticking") coefficient, which equals the number of "sticks" of a pollutant to a surface divided by the number of collisions with the surface. It was determined that the mass accommodation coefficients for ozone deposition onto these surfaces were in the range of  $10^{-5}$  to  $10^{-6}$ . Given this, an analysis was conducted to determine the relative effects of the transport and surface uptake resistances. It was found that for the surfaces tested in this study, the surface uptake resistance is rate limiting for mass accommodation coefficients on the low-end of the range, while boundary layer resistance is limiting for those on the high end of the range.

### INTRODUCTION

Tropospheric ozone has been identified as a criteria air pollutant by the Environmental Protection Agency, since it is known to cause acute health effects and there is evidence that it may be responsible for more severe chronic effects, (1). An individual's exposure to a pollutant such as ozone can be characterized as the sum of exposures in the microenvironments where the individual spends his or her time. One delineation of these microenvironments is outdoors versus indoors. It is known that ambient ozone infiltrates into residences, (2), resulting in indoor concentrations from about 20 to 80 percent of the outdoor concentration, (3). Considering that individuals spend about 90 percent of their time indoors, (3), it is clear that the indoor environment may constitute a significant ozone exposure.

One important tool in indoor air exposure assessment is the indoor air quality model. For ozone, one of the most important variables in these models is the deposition of ozone onto indoor surfaces. This deposition is the principal reason that indoor ozone concentrations are lower than outdoor concentrations. In this study, a chamber has been designed to study ozone deposition onto a variety of indoor surfaces. Also, the factors that affect ozone deposition, including room air flows and surface uptake, are analyzed.

### BACKGROUND

Deposition onto indoor surfaces is usually modelled through the concept of the deposition velocity. It is defined as the rate of decay of the pollutant divided by its mean concentration in air, (4), and can be written as,

$$K_d = \frac{F}{C} \quad (1)$$

where  $F$  is the flux to the surface (units of mass deposited per area per time) and  $C$  is the free-stream concentration, which is assumed to be uniform throughout the indoor space. Use of the deposition velocity also assumes that the loss process is first-order.

For atmospheric deposition modelling, the flux depends on the convective and diffusive flows transporting the pollutant to the surface (e.g. ground, building surfaces, etc.) and the uptake of the pollutant at the surface. For this reason, the deposition velocity can be written as the combination of three

resistances: the aerodynamic resistance,  $r_a$ ; the boundary layer resistance,  $r_b$ ; and, the surface uptake resistance,  $r_c$ , as, (5):

$$K_d = \frac{1}{r_a + r_b + r_c} \quad (2)$$

The first resistance term accounts for the mixing of the pollutant in the core region above the boundary layer. This term is generally independent of the pollutant. Rather it is determined by the wind speed and turbulence. The second term corresponds to the movement of the pollutant across the boundary layer to the surface. This resistance is related to the diffusion coefficient of the pollutant and the thickness of the boundary layer. Finally, the surface uptake resistance corresponds to the rate of pollutant uptake at the surface and depends on the nature of the absorbate (i.e. the pollutant) and the absorbent (i.e. the surface).

This analogy can be extended to indoor pollutant deposition with some modifications. Indoor air flows are often assumed to follow the boundary layer assumption, in which the air away from the surface (the core region) of an enclosure is assumed to be an ideal fluid while the air near the surface (i.e. in the boundary layer) is assumed to be a viscous fluid. The air flow in the core region is normally circulating along the periphery of the enclosure, essentially parallel to the wall. Thus, this air flow does not constitute a transport mechanism to the surface and there is no aerodynamic resistance. For indoor pollutant deposition, the important resistances are the boundary layer and surface uptake resistance. Ozone is a highly reactive gas, and it is assumed that once it is taken up by the surface it immediately reacts. Thus, the mass accommodation coefficient, which is defined as the number of collisions of a gas molecule and a surface resulting in a "stick" divided by the number of collisions, will be used to examine the surface uptake resistance. Low values of the mass accommodation coefficient indicate that the surface uptake resistance is important. The mass accommodation coefficient for several ozone-surface reactions was determined in this study.

## MATERIALS AND METHODS

### Description of the Apparatus

The apparatus for the deposition experiments is a laminar flow reactor. Air with ozone (generated by a UV Photometric Ozone Calibrator) flows through a cylindrical glass test section. Ozone is measured with Monitor Labs Model 8410 chemiluminescent ozone analyzers before and after the test section to determine the ozone deposition. Continuous measurements of the temperature and relative humidity in the test section are made using temperature and relative humidity probes (Omega 411). The flow rate through the test section is monitored with a calibrated rotometer. The test section has an inside diameter of 2.1 cm and is 30 to 60 cm length. Several materials that are commonly found on indoor surfaces were tested including latex paint, vinyl wallpaper and paper wallpaper. For latex paint the inside of the test section was simply painted while the wallpaper was glued to the inside of the test section. At this point, only one brand of latex paint has been tested. Ozone deposition, defined as the percent of ozone depositing on the test section, was measured over a range of relative humidities. For a more detailed description of the apparatus see reference (6).

### Mass Accommodation Coefficient Calculation

McMurray and Stolzenburg (7) provide the model for measuring mass accommodation coefficients from laminar tube flow. For a gas penetrating in a cylindrical tube with fully-developed laminar flow, the appropriate steady-state convective transport equation is the following,

$$2u \left( 1 - \left( \frac{r}{r_0} \right)^2 \right) \frac{\partial C}{\partial z} = D_g \left( \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial C}{\partial r} \right) + \frac{\partial^2 C}{\partial z^2} \right) \quad (3)$$

where  $C(r,z)$  is the concentration of the pollutant species,  $r$  is the radial distance from the center of the tube,  $r_0$  is the tube radius,  $z$  is the axial distance,  $D_g$  is the pollutant diffusion coefficient in air and  $u$  is the mean flow speed in the axial direction.

The term on the left side of equation (3) represents the bulk flow while the term on the right side represents diffusive flows, both radial and axial. However, it can be shown that the axial diffusion is

negligible. Porous diffusion into the surface was also neglected because it is assumed that ozone reacts immediately upon being adsorbed onto the surface. The following boundary conditions apply to our system, (7),

$$C(r,0) = C_0 \quad (4)$$

$$\frac{\partial C}{\partial r} \Big|_{r=0} = 0 \quad (5)$$

$$-D_g \frac{\partial C}{\partial r} \Big|_{r=r_0} = \frac{\alpha v C(r_0, z)}{4} \quad (6)$$

where  $\alpha$  is the mass accommodation coefficient and  $v$  is the mean thermal speed of the pollutant molecule. Equation (4) simply states that the inlet concentration is  $C_0$  at all  $r$ . Equation (5) states that the concentration is maximized in the radial direction at  $r=0$  (i.e. the center of the tube) and assumes symmetry around the tube center-line. Equation (6) states that the net diffusional flux to the surface equals the rate of uptake, which is calculated from the kinetic theory of gases. It also assumes that the re-release of ozone from the surface can be neglected because ozone is highly reactive. McMurray and Stolzenburg (7) provide the solution to this system. It was used to determine the mass accommodation coefficient given an experimentally determined deposition.

## RESULTS AND DISCUSSIONS

Table 1 shows selected results from the chamber study. For a more detailed presentation of the chamber study results see reference (6). The mass accommodation coefficients ranged from about  $10^{-6}$  to  $10^{-5}$ . This indicates that ozone reacts once in every one hundred thousand to one million collisions with a surface. Also, the relative humidity had a large effect on deposition onto latex paint. For low relative humidities, the mass accommodation coefficient was on the order of  $1 \times 10^{-6}$ , while for high relative humidities, the mass accommodation coefficient is about  $5 \times 10^{-6}$  to  $2 \times 10^{-5}$ . This indicates that at high relative humidities there is about 5 to 10 times as many "sticks" to the surface per collision than at low relative humidities. For glass and vinyl and paper wallpaper, the relative humidity had no effect on the deposition.

Traditional thought regarding surface wall deposition modelling envisions a pollutant from the bulk air diffusing across the boundary layer to the wall. Modelling this system can be very difficult because of the complexity of indoor air fluid dynamics. This approach is necessary for large particles, which have small diffusion coefficients, and, thus, the deposition may be limited by the boundary layer transport. Also, while small particles have larger diffusion coefficients, they normally stick upon every collision. On the other hand, gases may stick much less readily, and the uptake process may be the rate limiting step. In this case, the resistance to uptake at the wall is much greater than the transport resistance to the wall and the deposition can be modeled by knowledge of only the physics of random molecular motion. This can be done with the well known laws of the kinetic theory of gases, (e.g. (8)).

As a concrete example, consider the following residential environment: a 5m x 5m room with a 2.5m ceiling. The side walls are covered with a latex paint. All deposition will be assumed to occur on these walls. The resistances for the two corresponding processes will be calculated. The derivation of these resistances is provided in reference (9) and references therein.

### Boundary Layer Characteristic Time

The boundary layer resistance can be calculated as follows,

$$r_b = \frac{\delta}{D_g} \quad (7)$$

where  $\delta$  is the thickness of the boundary layer and  $D_g$  is the diffusion coefficient of the gas in air, (7). The thickness of the boundary layer in indoor environments can be estimated by assuming air flows uniformly along the length of the room using the following equation, (10),

$$\delta = \frac{L}{Sh_L} \quad (8)$$

where  $Sh_L$  is the dimensionless Sherwood number and  $L$  is the length of the surface in the direction of the air flow. The Sherwood number for flow past a flat plate can be calculated by its relationship to two other dimensionless numbers, the Reynolds and Schmidt numbers. The Reynolds number is a function of the air velocity, which will change under different residence conditions. The equations for performing this calculation are readily available in the literature, (e.g. (11)).

We are concerned with the case where the boundary layer resistance is highest. This occurs when there is low air flow. Assuming flow parallel along the length of the walls, one can estimate the lowest possible average air flow for a residence by dividing the infiltration rate by the cross-sectional flow area. A tight residence may have an air exchange rate of around  $0.5 \text{ hr}^{-1}$ . For our case, the volume of the room is  $62.5 \text{ m}^3$  ( $5\text{m} \times 5\text{m} \times 2.5\text{m}$ ). Multiplying the volume by the air exchange rate gives  $31.25 \text{ m}^3/\text{hr}$  for the infiltration rate. This number is divided by the cross-sectional flow area ( $12.5 \text{ m}^2$ ) to give  $2.5 \text{ m/hr}$  or  $0.07 \text{ cm/sec}$ . From the method above, this translates into a boundary layer of  $50 \text{ cm}$  and a  $323 \text{ sec/cm}$ . However, this situation is seldom, if ever, realized in actual indoor environments. There are typically thermal gradients within residences that result in much higher free-stream velocities. Matthews et al. (12) measured a median air velocity in six homes of  $5.3 \text{ cm/sec}$ . This translates into a boundary layer of  $5.7 \text{ cm}$  and a resistance of  $37 \text{ sec/cm}$ . Also, Matthews et al. report that the lowest median air velocity measured in a single room was  $1.1 \text{ cm/sec}$ . This air velocity gives a boundary layer of  $13 \text{ cm}$  and a  $84 \text{ sec/cm}$ . A high end air velocity for a residence may be about  $10 \text{ cm/sec}$ , which gives a boundary layer of  $4.2 \text{ cm}$  and a resistance of  $27 \text{ sec/cm}$ .

### Surface Uptake Characteristic Time

The surface uptake resistance onto a single wall in the enclosure can be calculated as follows,

$$r_s = \frac{4}{v\alpha} \quad (9)$$

where  $v$  is the mean thermal speed in the direction of the wall. The mean thermal speed can be determined from the kinetic theory of gases as, (8),

$$\bar{v} = \sqrt{\frac{8k_b T}{\pi m}} \quad (10)$$

where  $k_b$  is the Boltzmann constant,  $T$  is the absolute temperature and  $m$  is the mass of the pollutant molecule. At  $25^\circ\text{C}$  this gives  $362 \text{ m/sec}$  for the mean thermal speed.

For a low-range relative humidity experiment with a latex paint surface, the ozone mass accommodation coefficient was determined to be on the order of  $1 \times 10^{-6}$ . In this case, the surface uptake resistance is  $110 \text{ sec/cm}$ . For a mid-range relative humidity experiment (i.e. 50 percent), the ozone mass accommodation coefficient was found to be on the order of  $5 \times 10^{-6}$ . This gives a resistance of  $22 \text{ sec/cm}$ . Similarly, for a high-range relative humidity (i.e. 80 percent), the mass accommodation coefficient is about  $2.0 \times 10^{-5}$ , which gives  $5.5 \text{ sec/cm}$  for the resistance. If this was a glass room, the mass accommodation coefficient would be about  $5 \times 10^{-7}$ , which gives a resistance of  $221 \text{ sec/cm}$ .

### Implications of Characteristic Time Analysis

The resistances are summarized in Table 2. The low-range relative humidity experiment has a surface uptake resistance that is higher than all of the boundary layer resistances, except the theoretical low-end air velocity case. However, the boundary layer resistances are not negligible for the three air flow cases. This indicates that the surface uptake process is the major process for deposition onto low relative humidity latex paint surfaces; however, it is not rate limiting. The boundary layer resistance must be considered. For the mid-range relative humidity, the surface uptake process is about equally important as the boundary layer transport for the median and high-end case. For the high relative humidity case, the boundary layer resistance is rate limiting. Also, for glass, the surface uptake is rate limiting for the median and high-end air velocity cases.

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Table 1. Summary of Ozone Deposition Results

Experiment No.	Surface	Relative Humidity (percent)	Ozone Deposition (percent)	Mass Accommodation Coefficient
1	Latex Paint	4	4	$9 \times 10^{-7}$
2	Latex Paint	41-46	9	$2.2 \times 10^{-6}$
3	Latex Paint	53-56	20	$5.6 \times 10^{-6}$
4	Latex Paint	79-85	44	$1.9 \times 10^{-5}$
5	Latex Paint	66-71	25	$7.5 \times 10^{-6}$
6	Vinyl Wallpaper	6-7	15	$3.9 \times 10^{-6}$
7	Vinyl Wallpaper	68-75	21	$5.9 \times 10^{-6}$
8	Paper Wallpaper	6-9	5	$1.2 \times 10^{-6}$
9	Paper Wallpaper	67-71	4	$9 \times 10^{-7}$
10	Paper Wallpaper	73-77	3	$7 \times 10^{-7}$

Table 2 - Summary of Resistances

Resistance Term		Resistance (sec/cm)
Boundary Layer	Theoretical Low-End Air Velocity	323
	Typical Low-End Air Velocity	84
	Typical Median Air Velocity	37
	Typical Median Air Velocity	27
Surface Uptake	Low-Range Humidity Latex Paint	110
	Mid-Range Humidity Latex Paint	22
	High-Range Humidity Latex Paint	5.5
	Glass	221

## EXPOSURE MODELING OF ACID AEROSOLS

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### ABSTRACT

The U.S. Environmental Protection Agency (EPA) is conducting an intensive characterization and human exposure monitoring program of acid species and related air pollutants in an urban environment. The EPA's Atmospheric Research and Exposure Assessment Laboratory (AREAL) in cooperation with the Harvard School of Public Health and the Philadelphia Air Management Laboratory is conducting field measurements in Philadelphia, Pennsylvania to: 1) characterize the spatial and temporal variations of acid aerosol species in an urban environment, 2) investigate the complex chemistry of acid aerosols and other acidic species, including formation/removal mechanisms, and 3) provide acidic aerosol and particulate data base for exposure modeling and a study of pollution health effects.

One of the goals of the EPA's aerosol acidity study is to develop models of human exposure to acid aerosol species. Exposure models will be used to estimate the distribution of human exposures to acid aerosols. The models would be an important planning tool for assessing exposures by: 1) determining acid aerosol exposures in high-risk groups, 2) facilitating planning of subsequent sampling strategies, and 3) evaluating the effectiveness of proposed or implemented mitigation efforts on reducing human exposures to acid aerosols.

This paper focuses on issues to be addressed in developing models of human exposure to acid aerosols. The intent is to describe a sampling scheme that provides the information needed for development of an acid aerosol exposure model.

### INTRODUCTION

Concern over the health effects from acid aerosols has increased in recent years. Evidence exists linking exposure to acid aerosols with adverse health effects in humans.<sup>1</sup> Especially susceptible are individuals who suffer from respiratory ailments, including asthmatics and those with chronic bronchitis. Young children and the elderly are also susceptible.

To address the concern over a health risk from exposure to acid aerosols, the U.S. Environmental Protection Agency (EPA) is conducting an intensive characterization and human exposure monitoring program of acid species and related air pollutants in an urban environment. The EPA's Atmospheric Research and Exposure Assessment Laboratory (AREAL) in cooperation with the Harvard School of Public Health and the Philadelphia Air Management Laboratory is conducting field measurements in Philadelphia, Pennsylvania to:

- characterize the spatial and temporal variations of acid aerosol species in an urban environment,
- investigate the complex chemistry of acid aerosols and other acidic species, including formation/removal mechanisms,
- provide acidic aerosol and particulate data base for exposure modeling and a study of pollution health effects.

Philadelphia is the first city in the multi-city Metropolitan Aerosol Acidity Characterization Study (MAACS) which will enable characterization of acid aerosol exposures on a regional scale.

One of the goals of the EPA's aerosol acidity study is to develop models of human exposure to acid aerosol species. Exposure models will be used to estimate the distribution of human exposures to acid aerosols. The models would be an important planning tool for assessing exposures by: 1) determining acid aerosol exposures in high-risk groups; 2) facilitating planning of subsequent sampling strategies; and 3) evaluating the effectiveness of proposed or implemented mitigation efforts on reducing human exposures to acid aerosols.

This paper focuses on issues to be addressed in developing models of human exposure to acid aerosols. The intent is to describe a sampling scheme that provides the information needed for development of an acid aerosol exposure model.

## BACKGROUND

The Philadelphia aspect of the MAACS has four primary parts, all of which are important to developing an exposure model. The first is to assess the spatial and temporal character of acid aerosol concentrations through a network of fixed-site monitoring stations that are upwind, downwind, and throughout the Philadelphia metropolitan area. Information obtained from this aspect will provide valuable input to exposure model development by aiding in the determination of the effect of population and degree of urbanization on local acid aerosol concentrations. Information on diurnal variations of acid aerosol concentrations will be an important parameter for model development as well. Sampling strategies must take into account the variable nature of acidic aerosols where both minimum and maximum concentrations typically occur between 8:00 am and 8:00 pm.<sup>2</sup> Hence, a 12-hour sampling period would span both the minimum and maximum ambient H<sup>+</sup> concentrations.

The second aspect involves detailed measurements of acid aerosol concentrations during the summer months. Information on formation and removal mechanisms, neutralization of particle strong acid (H<sup>+</sup>) by ammonia, and neutralization by ammonium salts are gathered during this period. The information gathered on concentration and duration of acid aerosol episodes is needed to determine the proper averaging time for sample collection based on health responses and transport and conversion processes. This information will be vital to developing an exposure model which accurately estimates a population's exposure when acid aerosol concentrations are typically at their highest levels.

The third component of the study includes the collection of data needed to perform exposure analyses. Ambient, indoor, and personal measurements of acid species and related pollutants will be collected in a time period that is consistent with both the reactive chemistry of the pollutants and the health response from exposure to the acid aerosols. For calculation of exposure, various microenvironments (both indoors and outdoors) are being characterized for key pollutants to determine levels and an appropriate sampling schedule. Variation in pollutant concentration due to seasonal and diurnal effects is also being defined. Activity-pattern information can be obtained from previous studies of human activity,<sup>3,4,5</sup> or by tracking the daily activities of the individuals wearing a personal exposure monitor (PEM) in each city for a site-specific account of exposure. Of particular importance is the frequency and duration with which susceptible groups (e.g., asthmatics and individuals with chronic respiratory disease) come into contact with acid aerosols.

The fourth component of the study will be testing of an integrated weekly sampling approach. Model requirements will be developed which will be considered in the planning of field studies in the other cities in the MAACS and future field studies as well. The sampling protocol for these future studies needs to be consistent with the model requirements to be developed.

### Preliminary Modeling of Indoor Acid Aerosol Concentrations

A model for estimating indoor concentrations of H<sup>+</sup> was developed from a study that estimated indoor exposures of children using air pollutant concentrations measured at a single stationary ambient monitoring (SAM) site.<sup>2</sup> In the above mentioned study, the estimated acid aerosol concentrations were compared to measurements collected at the SAM site. Factors that influenced indoor and personal concentrations were identified and incorporated into the acid aerosol model.

The predictive model for indoor H<sup>+</sup> concentrations is given by:

$$H^+ = [H^+]_{OUT} - \left( [H^+]_{OUT} * kSO_4^- \right) - \left( [H^+]_{OUT} * kSO_4^- * kNH_3 * [NH_3]_{IN} \right) \quad (1)$$

where H<sup>+</sup> (nmol/m<sup>3</sup>) is the estimated indoor concentration, H<sup>+</sup><sub>OUT</sub> (nmol/m<sup>3</sup>) is the measured outdoor concentration, kSO<sub>4</sub><sup>-</sup> is a dimensionless term representing the fraction of particles that deposit on indoor surfaces or that fail to penetrate indoors, and kNH<sub>3</sub> \* NH<sub>3</sub><sub>IN</sub> is the first-order reaction rate of H<sup>+</sup> with NH<sub>3</sub>. Equation (1) shows that to estimate indoor H<sup>+</sup> requires information on the concentration of outdoor H<sup>+</sup>, the indoor NH<sub>3</sub> concentration, the loss rate for sulfate, and the reaction coefficient for the reaction of H<sup>+</sup> with NH<sub>3</sub>.

### Factors Affecting Acid Aerosol Concentrations

A study on personal exposure modeling of aerosol strong acidity in Uniontown, Pennsylvania, during the summer of 1990 (Suh *et. al.*<sup>2</sup>) found among other results that: 1) there was little to no spatial variation in outdoor H<sup>+</sup> concentrations within Uniontown, 2) there was significant diurnal variation in outdoor H<sup>+</sup>, 3) personal H<sup>+</sup> exposure levels were generally higher than indoor concentrations and lower than outdoor concentrations with the differences being quite pronounced, 4) outdoor concentrations of H<sup>+</sup> were unable to account for interpersonal variability in personal H<sup>+</sup> exposures, 5) time-weighted microenvironmental models predicted personal exposures for H<sup>+</sup> better than outdoor concentrations alone, and 6) indoor concentrations of H<sup>+</sup> appeared to be affected by the use of air conditioning because of its effect on concentrations of gaseous ammonia or ammonium salts.

The reactive chemistry of acid aerosols and ammonia must be included in both indoor concentration and personal exposure models of acid aerosols. Individual species must be characterized. Ammonia and acid particles do not coexist, however, they could each be present in appreciable amounts at different times during a multi-hour sampling period.<sup>6</sup> Therefore, an integrated sample collected over several hours may collect both acid particles and ammonia, thus hiding the true interaction between these chemical species and making modeling of exposures very difficult.

Health effects associated with acid aerosols are primarily due to exposure to fine (aerodynamic diameter  $\leq 2.5$   $\mu\text{m}$ ) particles. For modeling purposes, it is important to discriminate by particle size. This is particularly true for indoor concentrations. Particle size and density, deposition on indoor surfaces, reaction rates with other indoor pollutants, volume of home, and air exchange determine the indoor decay rate of pollutants originating from outdoor sources.<sup>7</sup> Information on housing stock-type and ventilation characteristics may aid in explaining differences between indoor and outdoor concentrations of acid aerosols and other key pollutants.

For pollutants such as acid aerosols which are characterized by considerable infiltration into homes, it is necessary to carefully measure the variation of both indoor and outdoor concentrations for use in an exposure assessment. It has been seen that ambient levels of pollutants with high infiltration rates significantly affect personal exposures even where indoor sources are present.<sup>8</sup> Measurements taken in both indoor and outdoor environments are in addition to personal sampling. All three types of samples being necessary to characterize and model the spatial and temporal variation of acid and related aerosols.

An exposure model for acid aerosols must incorporate the reactive chemistry of acid species, particularly with respect to either co-existence or neutralization by ammonia. Infiltration of fine acid sulfate particles to the indoor environment needs to be included. Once indoors, heterogeneous processes such as reactions with indoor surfaces and deposition, needs to be accounted for by the model. Detailed information on the interaction between people conducting their daily routines and airborne acid concentrations in outdoor and indoor microenvironments is vital for exposure modeling. Particularly important is time-location and activity data for persons with chronic bronchitis, asthmatics, and other subsets of the population most susceptible to inhalation of acid aerosols.

### RECOMMENDATIONS

Considering the factors from the previous section which affect the spatial and temporal distribution of acid aerosols, and the findings of Suh and co-workers<sup>2</sup> (also in the section above), the following list of recommendations needs to be considered when planning future exposure studies for acid aerosols.

- Indoor/outdoor (I/O) ratios of acid aerosols are needed to conduct exposure modeling. Therefore, indoor measurements of acid aerosols as well as outdoor measurements will be required to model personal exposures to acid aerosols.
- Ammonia levels and sources should be characterized.
- Additional studies of the interactions between H<sup>+</sup> and NH<sub>3</sub> are needed, especially in the breathing zone of a person. Also, information is needed on loss of particles in the immediate vicinity of a person's body.
- Air exchange and room volume measurements for each dwelling are needed particularly in light of the fact that H<sup>+</sup> particles are primarily from outdoors.

- Sampling should take place on a short enough temporal scale to monitor the variation in outdoor and indoor acid aerosol concentrations.
- Personal exposure sampling should be conducted since interpersonal variability in acid aerosol concentrations can be large.<sup>2</sup>

### Sampling Protocol

The above recommendations would be expressed through the following protocol of sampling for acid aerosols.

#### Sample duration:

Indoors: 24-hour sampling with a resolution of no more than 3 hours (1-hour samples would be preferable).

Outdoors: Same schedule as indoors.

Personal: Samples with the shortest sampling duration achievable (preferably no longer than 3-hour samples).

The sampling schedules described above may not be appropriate given current measurement capabilities.

Sampling which is not able to achieve the limit of detection (LOD) for a chemical species should not be done. But, as sampler technology and analytical methods improve, and the LOD for key species is lowered, shorter sampling durations should be used.

#### Sample frequency:

Indoors and personal: Every day (24 hours).

Outdoors: Every second day (24 hours).

After analyzing data from the Harvard Acid Aerosol and Six-Cities Studies for seasonal and spatial variability of aerosol acidity, Thompson *et. al.*<sup>9</sup> determined that outdoor samples collected every other day provided adequate information on annual averages and medians. Therefore, sampling outdoors every other day would be acceptable.

#### Primary measurements:

1. Aerosol strong acidity ( $H^+$ ) and ammonia ( $NH_3$ ).
2.  $SO_4^-$ ,  $NO_3^-$ ,  $NH_4^+$ , O<sub>3</sub>, HONO, HNO<sub>3</sub>, SO<sub>2</sub>, and NO<sub>2</sub>.
3. PM<sub>2.5</sub> and PM<sub>10</sub>.

#### Other:

1. Complete characterization of dwelling including: number and orientation of rooms, square footage, number of windows, air-conditioning, etc.
2. Air exchange measurements across the indoor/outdoor interface for various housing stock and building types.
3. Ventilation data for indoors.
4. Time/location activity patterns for individuals wearing a personal exposure monitor (PEM). It would be beneficial to obtain time-activity profiles for representative subgroups of the population whether they carry a PEM, or not.

### SUMMARY

The U.S. EPA's Atmospheric Research and Exposure Assessment Laboratory is conducting research into the characterization of aerosol acidity and related chemical species with emphasis on their relationship to human exposure. Exposure modeling of acid aerosol will play an important role in estimating the exposures experienced by urban populations. The modeling of human exposures to acid aerosols requires detailed information on the spatial and temporal distribution of  $H^+$  and other relevant chemical species. Data on human activity patterns is also required. As yet there are still many unanswered questions regarding the atmospheric and chemical processes that affect aerosol acidity and the impact of aerosol acidity on human health. Exposure modeling of  $H^+$  will be an invaluable tool for assessing the distribution of exposures experienced by an urban population and for identifying population subgroups that are most at risk from exposure to aerosol acidity.

In this paper we have tried to identify the physical parameters needed for developing a human exposure model for acid aerosols. A rigorous sampling protocol has been outlined which is appropriate for collecting the level of information needed for model input. Future exposure studies of acid aerosols should incorporate as much of the sampling protocol outlined here as possible in their study design.

#### **ACKNOWLEDGEMENTS**

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*Session 3*

*Measurement of Semi-Volatile*

*Organic Compounds*

## **The Distribution of Semi-Volatile Organic Compounds Between the Vapor and Particulate Phases: Diffusion Denuder Measurements**

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### **ABSTRACT**

Collection of particles on a filter results in under-estimation of particulate organic compounds due to losses from the semi-volatile organic fraction during sample collection, i.e. a "negative sampling artifact." This sampling induced change in the phase distribution of semi-volatile organic material results in the loss of about half of the particulate organic material during sampling. These semi-volatile organic compounds lost from particles can be correctly measured using a diffusion denuder sampling system. A multi-system, multi-channel, high-volume diffusion denuder sampler has been used for the determination of the particle size distribution and chemical composition of semi-volatile organic compounds in fine particles in two urban environments, Los Angeles and Philadelphia. Organic compounds lost from the particles included paraffinic compounds, aromatic compounds, and organic acids and esters. Underestimation of the composition of semi-volatile organic compounds in particles is a function of molecular weight, chemical compound class and particle size. The majority of the organic compounds in fine particles 0.8 to 2.5  $\mu\text{m}$  in size are semi-volatile organic compounds lost from the particles during sampling onto a filter. The majority of carbonaceous material in particles smaller than 0.4  $\mu\text{m}$  is not lost from the particles during sampling.

### **INTRODUCTION**

Correct assessment of the exposure of a population to particulate organic material is in part dependent on accurate determination of the chemical composition as a function of particle size for particles present in the atmosphere. Results obtained from the collection of organic material on a filter indicate that about one-third of the mass of fine particulate matter (diameter < 2.5  $\mu\text{m}$ ) collected on filters in remote desert regions of the Southwest U.S. (Macias 1986, Sutherland 1990) and about one-fourth of the fine particulate mass in western urban areas such as the Los Angeles Basin (Hering 1993) is organic compounds and elemental carbon. In the Eastern United States, sulfate is the major component of airborne fine particles. However, based on filter data, organic material also comprises about one-fourth of the fine particulate mass in the east (Gebhart 1993). Collection of particles on a filter results in underestimation of particulate organic material due to losses from the semi-volatile organic fraction during sample collection, i.e. a "negative sampling artifact". This sampling induced change in the phase distribution of semi-volatile organic material results in the loss of about half of the particulate organic material during sampling (Eatough 1993, 1990, 1989, Tang 1993). This "negative sampling artifact" is an order of magnitude larger than the "positive sampling artifact" resulting from the collection of organic compounds by a quartz filter (Eatough 1993, Appel 1989, McDow 1990).

The loss or gain of significant amounts of semi-volatile organic material from particles or the sampling media during sampling causes errors in the determination of aerosol chemical composition. Accurate collection procedures for semi-volatile organic compounds must meet the following two criteria.

1. Organic compounds initially present in the gas phase must not be adsorbed onto particles or the filter during sampling.
2. Organic compounds initially present in the particulate phase must be captured during sampling separate from compounds which are present in the gas phase in the atmosphere.

These two criteria cannot be met by any sampling procedure in which the particulate phase organic compounds are collected before the collection of gas phase organic compounds because the gas phase organic compounds and organic compounds volatilized from particles become indistinguishable. Thus, it is necessary to first remove the gas phase organic compounds and then to collect the particulate phase organic compounds with a sampler which will collect all organic material, gas and particle.

This paper described the results obtained using a high-volume, multi-system, multi-channel diffusion denuder sampling system (Tang 1993) (BIG BOSS) and associated analytical procedures for the determination of the size distribution and chemical composition of fine particulate organic material. Details are given on the chemical composition and concentration of semi-volatile organic compounds retained by and lost from particles during sampling for samples collected in the Los Angeles urban area. Results obtained from capillary column-gas chromatography, GC, analysis of collected samples are compared for samples from Los Angeles and Philadelphia sampling sites. Semi-volatile particulate organic compounds present in samples collected at Los Angeles and Philadelphia are identified by GC-MS analysis.

## EXPERIMENTAL

### The BIG BOSS Sampling System.

The BIG BOSS sampling system has been previously described (Tang 1993). The BIG BOSS uses a variety of size selective virtual impactor inlets to control the particle size of the particles introduced to the diffusion denuder sampler. The components of the BIG BOSS are shown schematically in Figure 1. Systems 1, 2 and 3 are used to determine total particulate organic material after a diffusion denuder which removes gas phase organic compounds. Total flow through the denuder for each system is 200 L/min. The denuder for these three systems is preceded by a virtual impactor with particle size cuts of 2.5, 0.8 and 0.4  $\mu\text{m}$ , respectively (Tang 1993). The flow stream after the denuder is split and sampled through two parallel filter packs. The majority of the flow, 160 L/min, is sampled through a quartz filter followed by an XAD-II bed. Particles are collected by the quartz filter. Semi-volatile organic compounds lost from the particles during sampling are collected in the XAD-II bed. The material collected in this part of the sampling system is analyzed by GC and GC-MS to chemically characterize the organic material present in the particles and lost from the particles during sampling. The remainder of the sample flow, 40 L/min, is sampled through a filter pack with a quartz filter and a carbon impregnated filter, CIF. These filters are used for quantitative determination of total particulate carbonaceous material and semi-volatile compounds lost from the particles during sampling by temperature programmed volatilization, TPV, analysis (Eatough 1993, 1989, Tang 1993). The fourth system in the BIG BOSS, Figure 1, contains two quartz filters in front of the diffusion denuder. The data obtained with System 4 is used to correct the data from the other systems for any gas phase organic compounds not collected by the diffusion denuder.

### Sampling With the BIG BOSS.

The BIG BOSS has been field tested in two urban sampling programs. The first sampling program was completed during June 1992 in the Los Angeles Basin at the South Coast Air Quality Management District,

SCAQMD, sampling site in Azusa, CA. Representative results related to the identification of particulate semi-volatile organic compounds in samples collected at Azusa were included in the article describing the BIG BOSS (Tang 1993). Results are reported here for eight-hour samples (10:00 to 20:00 hours) collected on 16 consecutive days and four-hour samples collected twice a day (10:00 to 14:00, and 14:30 to 18:30) during the last three days of the sampling program at the SCAQMD Azusa sampling site. Samples were then collected during a one-week period in July 1992 at the North-East Airport Harvard University sampling site in Philadelphia, PA (Burton 1993). The total number of quality samples obtained at the Philadelphia site was limited to four samples because of inclement weather during part of the study.

#### Sample Analysis.

The samples collected during the two field sampling programs outlined above were analyzed to determine artifact-free particulate organic material in the particle size ranges of  $<0.4\mu\text{m}$ ,  $0.4\text{--}0.8\mu\text{m}$ , and  $0.8\text{--}2.5\mu\text{m}$  by both quantitative and qualitative analysis of the collected samples. Quantitative results for total particulate organic material in each of the three size ranges were obtained by TPV analysis (Eatough 1993, 1989). Semi-quantitative chemical characterization results for semi-volatile particulate organic material and the semi-volatile organic compounds lost from collected particles during sampling as a function of particle size have been determined by GC with FID detection (Tang 1993). The specific qualitative identification of the principal organic compounds lost from particles and semi-volatile organic compounds retained by particles during sampling has been done by gas chromatography-mass spectroscopy, GC-MS, analysis of combined samples. Examples of results obtained by each of these analyses are presented in this paper.

#### RESULTS AND DISCUSSION

Semi-volatile organic material is lost from particles during sample collection on a filter. The amount of particulate organic material on filter  $Q_{1,1}$  (the first quartz filter after the  $2.5\mu\text{m}$  inlet and denuder in System 1, Figure 1) agrees with that on filter  $Q_{4,1}$  (the first quartz filter after the  $2.5\mu\text{m}$  inlet in System 4) (Eatough 1993, Tang 1993). This agreement shows that the half-life for the loss of semi-volatile organic material from particles during sampling is much shorter than the sampling time so that the loss is comparable for particles collected on a filter before and after a diffusion denuder. This result also shows that the positive artifact resulting from the absorption of gas phase organic compounds by the quartz filter is minimal and that the gas-particle equilibrium is not significantly perturbed during passage through the denuder.

The data from the GC analysis of the material collected in the XAD-II beds or the TPV analysis of the charcoal impregnated filters of Systems 1-4, Figure 1, allow the determination of the particle size distribution of the semi-volatile organic material which was lost from the particles during sampling. The GC analysis of the material extracted from the XAD-II sorbent beds by dichloromethane gives a semi-quantitative measure of the various organic compounds captured by the XAD-II sorbent bed. This is illustrated by the data in Figure 2 where is shown the GC data obtained from analysis of the four sorbent beds for the sample collected on 14 June 1992. The amount of material on the XAD-II sorbent bed decreases in going from samples  $X_{1,1}$  through  $X_{4,1}$  Figures 1 and 2. The decreasing amounts seen in going from System 1 through System 3 reflects the decreasing amount of semi-volatile organic material lost from the particles as the inlet particle size cut is decreased from  $2.5\mu\text{m}$ , to  $0.8\mu\text{m}$ , and finally to  $0.4\mu\text{m}$ . The small amount of material seen for the  $X_{4,1}$  sorbent bed in Sampler 4 results from the incomplete collection of some gas phase organic compounds by the denuder. There is a slight tendency for the relative importance of the more volatile semi-volatile organic compounds lost from particles during sampling to increase with decreasing particle size, Figure 2. The organic compounds with longer GC retention times are more prominent in the Sampler 1 XAD data, indicating that these compounds are dominantly present in the atmosphere in the  $0.8\text{--}2.5\mu\text{m}$  particle size range. Organic compounds with short GC retention times dominate the organic material seen in the  $X_{4,1}$  sorbent bed (Figure 2), consistent with the expected incomplete collection of about 5% of the gas phase organic compounds by the diffusion denuder (Tang 1993).

The TPV analyses of the semi-volatile organic material captured by the CIF corresponding to each XAD sorbent bed, Figure 1, gives a quantitative determination of the total semi-volatile organic material lost from the particles and collected by the XAD-II sorbent bed or CIF filter after the denuder. The total integrated peak area of the GC data for each XAD-II collected sample is directly related to the amount of total evolved carbon determined from the TPV analysis, Figure 3. The correspondence between these two data sets provides a calibration of the GC results which may be used to quantitatively interpret the GC results obtained in the various parts of the sampling system.

The data for the amount of organic material collected by the XAD-II sorbent beds or the CIF sorbent traps in the first three sampling systems needs to be corrected for the denuder breakthrough measured in the XAD-II sorbent bed or CIF of the fourth sampling system to obtain the semi-volatile artifact as a function of particle size. This leads to the data shown as SVOC Lost in Figure 4 for the average particle size distribution of the semi-volatile organic material lost during the collection of particles for all of the sampling periods in the Los Angeles Basin study (Tang 1993).

The organic material determined by the GC analysis of the combined dichloromethane/methanol extraction (Tang 1993) of the quartz filters in front of the various XAD-II sorbent beds for Sampling Systems 1, 2 and 3 ( $Q_{1,1}$ ,  $Q_{1,2}$  and  $Q_{1,3}$  in Figure 1) is a measure of the semi-volatile organic material not removed from the particles during sampling. These results are also given in Figure 4 as Quartz SVOC. The TPV analysis of the corresponding quartz filters in the CIF filter pack for each system ( $Q_{2,1}$ ,  $Q_{2,2}$  and  $Q_{2,3}$  in Figure 1) gives the total carbonaceous material remaining on each quartz filter after sampling, Quartz C in Figure 4. The sum of Quartz C and Quartz SVOC gives the total particulate C, Particle C in Figure 4.

As indicated in Figure 4, the majority of the organic material in particles 0.8-2.5  $\mu\text{m}$  in size is lost from the particles during collection of the particles on a filter. About 80% of the carbonaceous material in the 0.8-2.5  $\mu\text{m}$  particles consists of semi-volatile organic compounds which are stripped from the particles during sampling. The semi-volatile organic material in particles 0.4-0.8  $\mu\text{m}$  in size is also essentially all lost from particles during sampling, Figure 4. However, about 60% of the total carbonaceous material in these particles is retained by the particles during sampling, Figure 4. In contrast, the great majority of the carbonaceous material in the particles smaller than 0.4  $\mu\text{m}$  is retained by the particles during sampling. These smallest particles are also the only size fraction with a significant amount of semi-volatile organic material remaining in the particles after collection of a sample, Figure 4. This regular trend of decreasing importance of the loss of organic material from particles with decreasing particle size probably results from a combination of two factors: 1. The concentration of elemental carbon increases with decreasing particle size. The increased amounts of "soot" in the <0.4  $\mu\text{m}$  size particles, as compared to larger fine particles, can be expected to result in the retention of some semi-volatile organic material in these particles due to strong absorption of the semi-volatile organic compounds by the graphitic structure of the soot. 2. The concentration of particulate secondary organic material produced from photochemical processes probably increases with decreasing particle size. This material will be rich in oxygen and nitrogen as a result of the photochemistry. The resulting organic material will be relatively non-volatile and would be expected to be retained by the particles during sampling.

We have previously reported data on the GC-MS identification of the semi-volatile organic material lost from particles during sampling for the sampling program in Los Angeles (Tang 1993). Compounds are present from all major organic compounds classes expected to be present in the atmosphere. For each compound class, the more volatile compounds predominate in the material lost from the particles and collected in the XAD-II bed during sampling. In contrast, the higher molecular weight organic compounds are retained by the particles during sampling. For example, particulate n-tetradecane and n-pentadecane are found only in the XAD-II bed and not in the particles after sampling. Hydrocarbons lower in molecular weight than these two compounds are found in comparable concentrations in the XAD-II beds of both Samplers 1 and 4, indicating they originate mainly from the breakthrough of some fraction of the gas phase component of these species. In contrast, n-tetracosane and higher molecular weight aliphatic hydrocarbons are retained by the particles during sampling and are not found in the XAD-II sorbent beds. Compounds of intermediate

molecular weight, e.g. n-decane, are partially lost and partially retained by the particles. Also illustrated by the GC-MS data is the increased tendency for lower molecular weight semi-volatile organic compounds to be retained by the particles during sample collection as the polarity of a given molecular weight compound increases. For example, n-heptadecane (MW 226) is largely lost from particles during sampling. However lauric acid (MW 214) and fluoranthene (MW 202) are largely retained by the particles during sampling.

The GC data obtained to the present indicate that the chemical composition of the semi-volatile compounds lost from particles during sampling was similar for samples collected at each of the two urban study sites, Los Angeles and Philadelphia, Figure 5. This probably reflects the importance of organic compounds from automotive emissions at each of these sites. Semi-volatile organic compounds lost from particles during sampling at both of the urban sampling sites included paraffins, aromatic compounds and organic acids and esters.

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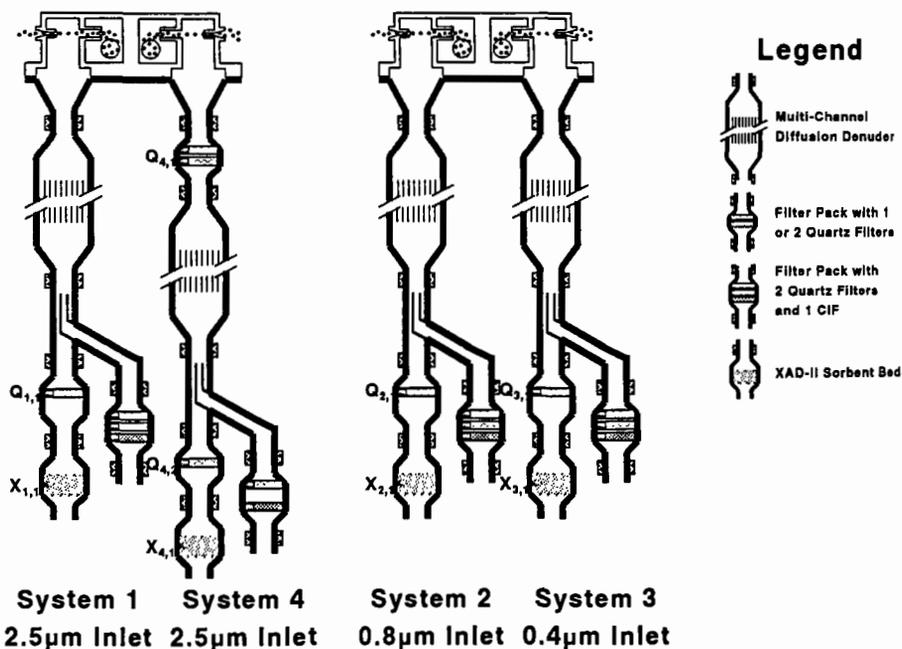


Figure 1. Schematic of the BIG BOSS sampling system, Sampler 1 (denuder, 2.5 μm inlet cut), Sampler 2 (denuder, 0.8 μm inlet cut), Sampler 3 (denuder, 0.4 μm inlet cut), and Sampler 4 (filter/denuder, 2.5 μm inlet cut).

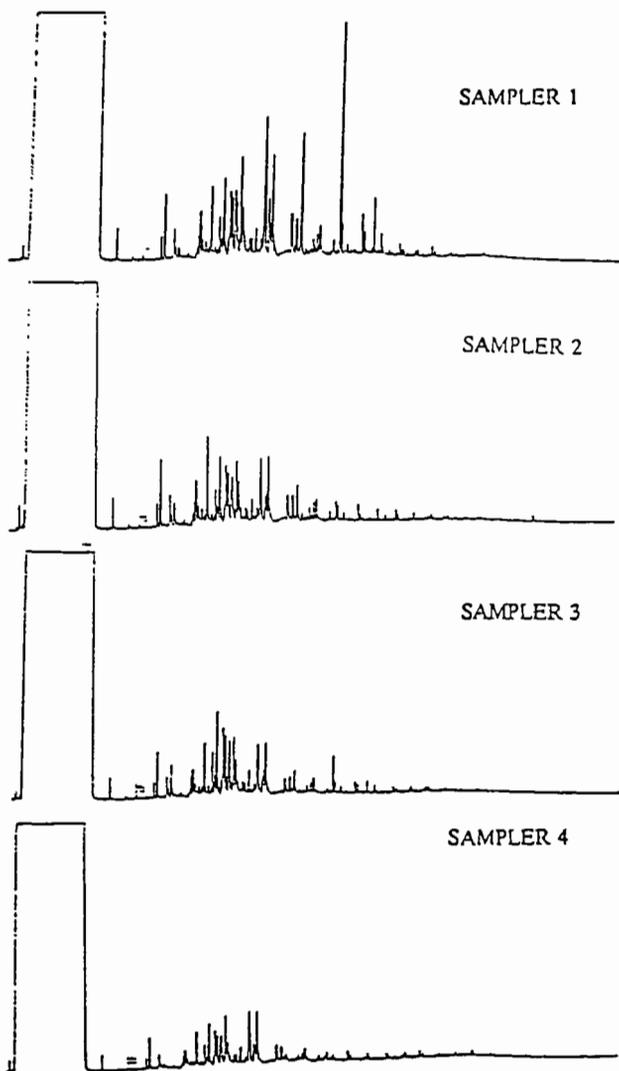


Figure 2. GC data for the organic compounds collected in the XAD-II beds after collection of particles in Samplers 1-4 of the BIG BOSS for samples collected from 10:00 to 18:00 pm June 14 in Los Angeles Basin (Azusa).

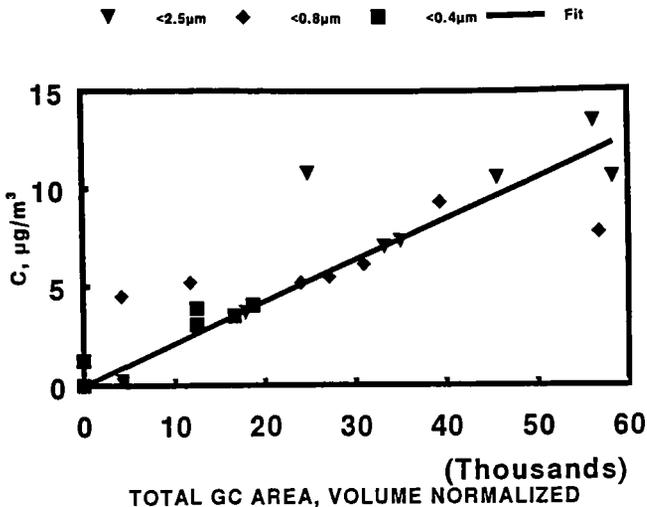


Figure 3. Comparison of the GC trace peak area for the organic material extracted from an XAD bed and the total collected semi-volatile organic C on the corresponding CIF filter of the BIG BOSS sampler.

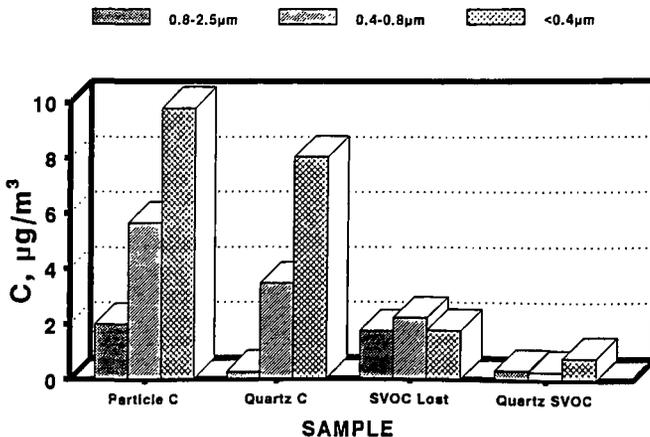


Figure 4. Fine particle size distribution of total carbonaceous material (Particle C), total carbonaceous material retained by particles during sampling (Quartz C), semi-volatile organic material lost from particles during sample (SVOC Lost) and semi-volatile organic material retained by particles during sampling (Quartz SVOC) for samples collected in the Los Angeles Basin.

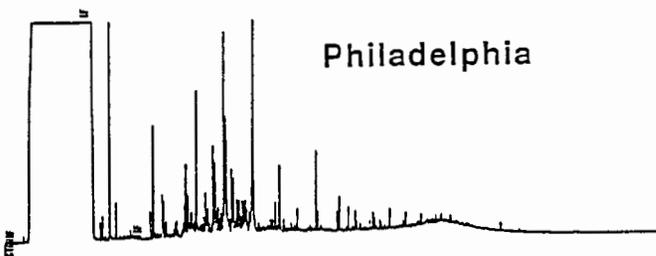
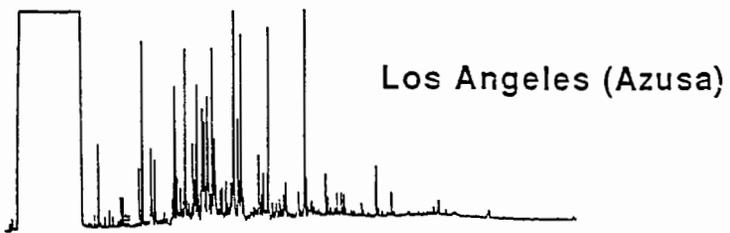


Figure 5. GC data for the organic compounds collected in an XAD-II bed after collection of particles in Sampler 1 of the BIG BOSS for samples collected in Los Angeles (Azusa) and Philadelphia.

**Use of a High-Volume Small Surface Sampler (HVS3)  
for the Microbiological Evaluation of Dust from  
Carpeted and Non-Carpeted Surfaces**

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A High-Volume Small Surface Sampler (HVS3) was previously developed through the U.S. Environmental Protection Agency (EPA) for the collection and analysis of lead and pesticides in surface dust ( $>5\mu\text{m}$ ) of carpeted and non-carpeted floors in residential buildings. At the request of EPA/Environmental Criteria and Assessment Office, Research Triangle Institute (RTI) has adapted the use of the HVS3 for the collection of surface dust for microbiological analyses. The major adaptations involve disinfecting the unit, and using sterile collection bottles. The collected dust samples are weighed, then sieved through a sterile, de-pyrogenated  $250\mu\text{m}$  screen. They are analyzed for mesophilic and thermophilic bacteria, fungi, mite guanine, and endotoxins. Dust samples were collected from routinely maintained carpet and tile floors in building "A", and "soiled" carpet from another building "B". Building A had dust loading levels of  $1.3\text{ g/m}^2$  on carpet and  $0.1\text{ g/m}^2$  on tile floors. Levels of endotoxin ( $0.2$  to  $6\text{ }\mu\text{g/g}$  of dust) and mite guanine were insignificant. Endotoxin levels were lower in the tile floor dust than the carpet dust. Mesophilic bacteria colony forming units (CFU) ranged from  $7.0 \times 10^4$  CFU/g (tile floor) to  $8.8 \times 10^6$  CFU/g (carpet), while thermophilic counts ranged from  $5.0 \times 10^2$  CFU/g (tile floor) to  $7.0 \times 10^3$  CFU/g (carpet). Fungi counts ranged from  $5.0 \times 10^3$  CFU/g (tile floor) to  $1.2 \times 10^5$  CFU/g carpet. In building B, dust levels were found to be higher at  $6.2\text{ g/m}^2$  of carpet. Mold and endotoxin levels were found to be higher in building B at  $3.2 \times 10^6$  CFU/g and  $103\text{ }\mu\text{g/g}$  respectively. The HVS3 can be used to measure dust microbiological loadings on surfaces. Additionally, bioaerosol monitoring will allow the relationship between surface and airborne microbial concentrations to be evaluated.

## BACKGROUND

The Research Triangle Institute (RTI) is currently performing a study with the Environmental Protection Agency's Environmental Criteria and Assessment Office (EPA/ECAO) to characterize biopollutants (both airborne and surface) for exposure assessments inside a building. A part of the study involves the investigation of levels of floor surface dust, its microbial composition, and its effect on indoor air. A method was needed for collecting floor surface dusts. A High Volume Small Surface Sampler (HVS3) was previously developed by the U.S. EPA's Atmospheric Research and Exposure Assessment Laboratory (EPA/AREAL) for the collection of residential carpeted and non-carpeted surface dust for pesticide and lead analysis.<sup>1,2</sup> The HVS3 is currently recommended for use in a draft ASTM method for the collection of dust for lead analysis. RTI has adapted procedures for using the HVS3 to collect dusts for microbiological analyses. The major adaptations involve disinfecting the unit, using sterile (steam autoclaved) polypropylene bottles to collect samples, and using Du Pont Hysurf® bags on the exhaust of the unit. For the first time, RTI has shown that the HVS3 can be used to collect surface dusts for the analysis of viable molds, yeasts, bacteria, endotoxins, and dust mite guanine. Preliminary data suggest that the HVS3 is useful in determining microbiological loadings on carpeted and non-carpeted surfaces. Use protocol development is currently ongoing and final results from the building biopollutant exposure study will be reported at a later time. This paper discusses a brief history of the HVS3, its characteristics, and some preliminary microbial results from two indoor environments.

## INTRODUCTION

The HVS3 utilizes a one horse power Royal® vacuum motor and a specifically designed nozzle and cyclone trap. The unit has Dwyer Magnehelic® gauges which are used to manually set the flow rate and pressure drop across the nozzle at the monitored surface. At the specified flow rate and pressure drop, the unit draws air at 20 cfm and has a 50% ( $D_{50}$ ) cutoff point of 5 microns. The cyclone effectively collects 99% of the dust lifted by the vacuum.<sup>3</sup> The dust collection efficiency has been reported to be approximately 93 to 97% from a smoothly painted surface, and averages 32%<sup>4</sup> on carpeted surfaces, dependent upon surface loading.<sup>2</sup> Du Pont Hysurf® bags, which are 98% efficient at 1 micron, are used on the exhaust of the unit. The Hysurf® bags are useful in determining whether bio-contaminants between 1 and 5 microns are exhausted from the cyclone during sampling.

## HVS3 OPERATION

### Cleaning and Leak Checking

Each part of the HVS3 which may come in contact with dust samples is thoroughly cleaned with a nylon brush, rinsed with hot water, and disinfected with 70% ethanol for 30 seconds. The pieces are dried with clean gauze and reassembled. A sterile, polypropylene bottle is attached to the cyclone. A leak-check is performed with a separate, Dwyer Magnehelic® gauge between a hose connector on the nozzle and one downstream near the flow control valve. The nozzle is closed with duct tape during the leak check. The unit must test less than 0.02 inches of water air flow to pass the leak check.

## Sampling

The area to be sampled is delineated with tape measures, and masking tape is used to mark the end lines of the area. The end lines are recommended to be at least one meter apart, and typically are extended by 0.5 meter increments up to 2 meters, depending upon the available space and the amount of sample required. The end line tapes are then evenly marked in 75 mm increments (3 inches) to create "lanes". The HVS3 is then placed on an end lane and the wheels are wiped with 70% ethanol. The unit is started, the flow rate and pressure drop is set, and a timer is started as the sample collection begins. The nozzle is passed over each lane between the end lines eight times (back and forth four times) at approximately 2 ft per second. Once the last lane is sampled in this manner, each lane is then passed over again as the sampler returns to the original end lane. At this point, the sampler and timer is stopped. The polypropylene bottle is removed, capped, labeled, and stored in a cooler. A data sheet is used to record the sample number, location, area, time sampled, and flow and pressure drop settings.

## SAMPLE PREPARATION AND ANALYSIS

### Sample Mass and Carpet Loading

The surface dust samples are collected in sterile, polypropylene bottles and returned to RTI laboratories in coolers for processing. The bottles are emptied and the mass of dust is recorded. The dust is loaded into a sterile, depyrogenated 250  $\mu\text{m}$  stainless steel sieve and mechanically shaken for 30 minutes. The dust mass fractions greater than 250  $\mu\text{m}$  and less than 250  $\mu\text{m}$  are calculated. Data from the sampling procedure are used to calculate the surface dust loading in grams per square meter.

### Fungi and Bacteria

The sieved bottom dust ( $\leq 250 \mu\text{m}$ ) is diluted ten and one hundred-fold, and the dilutions are plated on Sabouraud Dextrose Agar (SDA) plates for fungi (molds and yeasts), and Trypticase Soy Agar (TSA) for mesophilic and thermophilic bacteria. The SDA plates are incubated at 25°C for fungi, and the TSA plates are incubated at 32°C for mesophilic, and 55°C for thermophilic bacteria. After incubation, the colonies on the plates are counted and identified, and colony forming units per gram of dust are calculated.

### Endotoxin and Dust Mite Guanine

Endotoxin is a lipopolysaccharide (lps) component of gram negative bacteria cell walls. It is a respiratory irritant and can cause toxic effects. For endotoxin, the bottom dust is serially diluted and aliquots are reacted with an endotoxin specific lysate. The absorbance at 405 nm is read with a microtiter reader and is compared with the absorbance of a standard curve with known concentrations. The sample concentration is then calculated.

The presence of dust mites in dust samples are measured as a function of the presence of dust mite guanine. The sieved dust (250 mg) is placed through a series of extractions and reacted with guanase and xanthine oxidase. Other reagents are added and the absorbance of the final solution is read at 490 nm against controls with known concentrations.

## PRELIMINARY RESULTS

### Environments

The surfaces of two buildings designated as "A" and "B" were sampled with the HVS3. The floors in building A are routinely maintained and appear to be clean. Carpeted and tiled floors were monitored in building A. The carpeted floor surface of Building B did not appear to be routinely maintained and was noticeably "soiled." A carpeted floor was monitored in building B.

### Surface Dust Loading

Figure 1 shows the preliminary results of sampling with the HVS3. Initial carpet dust loading in building A was  $1.3 \text{ g/m}^2$  and the tile dust loading was  $0.1 \text{ g/m}^2$ . The carpet dust level in building B was higher at  $6.2 \text{ g/m}^2$ .

### Fungi and Bacteria

Figure 2 shows preliminary results of fungi in dusts collected with the HVS3. Fungi concentrations in building A were  $5.0 \times 10^3 \text{ CFU/g}$  in tile floor dust and  $1.2 \times 10^5 \text{ CFU/g}$  in carpet dust. The fungal concentration in building B carpet dust was higher at  $3.2 \times 10^6 \text{ CFU/g}$  carpet dust in comparison.

Preliminary mesophilic bacteria concentrations in building A were found to be  $7.0 \times 10^4 \text{ CFU/g}$  in tile floor dust and  $8.8 \times 10^6 \text{ CFU/g}$  in carpet dust, while thermophilic concentrations were found to be  $5.0 \times 10^2 \text{ CFU/g}$  in tile floor dust and  $7.0 \times 10^3 \text{ CFU/g}$  in carpet dust. The microbiological composition of the surface dusts from the buildings is similar to that of "ordinary" outdoor dirt. Microbial concentrations have initially been found to be higher in carpet floor dust than in tile dust.

### Endotoxin and Mite Guanine

Dusts in building A had insignificant levels of endotoxin. Figure 3 shows endotoxin concentrations found in surface dusts. Endotoxin levels found in dusts from building A ranged from  $0.2$  to  $6 \text{ } \mu\text{g/g}$  of floor dust. Endotoxin levels were lower in the tile floor dust than the carpet floor dust. Carpet from building B with a higher dust loading was found to have elevated levels of endotoxin at  $103 \text{ } \mu\text{g/g}$ . This level is considered to be elevated above expected levels found in carpet dust. Inhalation of a dose of  $20 \text{ } \mu\text{g}$  of endotoxin has been shown to induce a bronchial obstructive response in asthmatic subjects <sup>5</sup>.

Preliminary results showed that dust mite guanine was not detected in any of the dust samples.

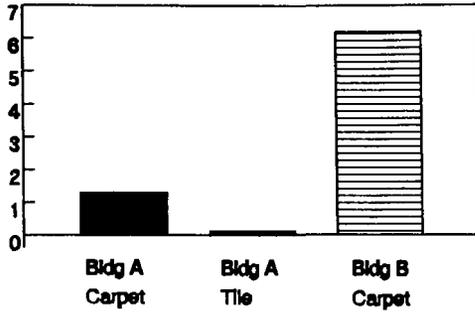


Figure 1. Surface Dust Loading (g/m<sup>2</sup>)

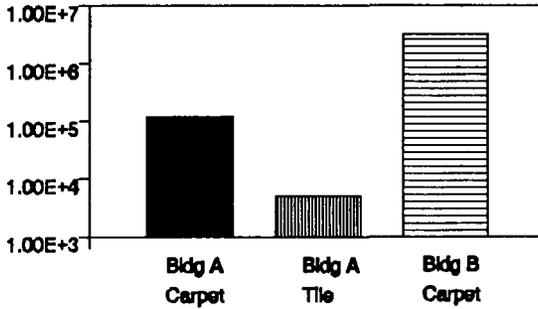


Figure 2. Fungi Concentrations (CFU/g of dust)

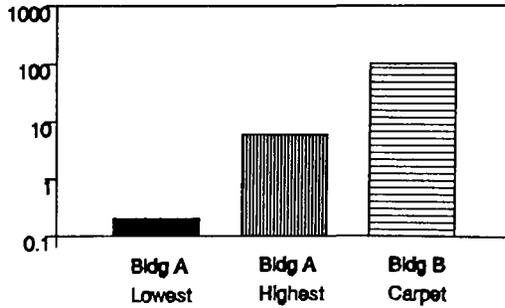


Figure 3. Endotoxin In Surface Dust

## CONCLUSIONS

Initial results indicate that the HVS3 can be used to effectively collect dust from carpeted and non-carpeted surfaces for a variety of microbiological analyses. The unit can be used to assess the dust loading and levels of microbiological contamination on floor surfaces. Further surface monitoring with the unit, along with concurrent bioaerosol monitoring, may yield information on the relationship between the microbial ecology of indoor surfaces and the microbiological contamination of indoor air.

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Methods for Polycyclic Aromatic Hydrocarbons  
and Tobacco Smoke Markers in House Dust: Laboratory and Field Evaluation

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#### ABSTRACT

Analytical methods were validated to determine polycyclic aromatic hydrocarbons (PAH) and other semivolatile organic compounds in house dust. We also examined the storage stability of three potential markers (solanesol, nicotine, and cotinine) for particulate-phase environmental tobacco smoke (ETS) in house dust. The results showed that less than 10 percent of the spiked solanesol was recovered from the dust after storage for 7 days in a typical indoor environment (room temperature and indoor lighting). Under the same storage conditions, after 21 days of storage, more than 90 percent of the cotinine and approximately 40 percent of the nicotine were recovered. These findings suggest that cotinine is a better marker for ETS particles in house dust than nicotine, whereas solanesol is not a suitable marker.

A small field study was conducted to evaluate the role of smokers in the house on the levels of PAH, cotinine, and nicotine present in house dust. Samples were collected from eight houses, using the High Volume Small Surface Sampler (HVS3) to collect carpet-embedded dust from designated areas in the carpet in either the living room or family room of each house. After collection, the dust samples were separated into fine ( $< 150 \mu\text{m}$ ) and coarse fractions. Most of the dust loading (69-85 percent) was found to be distributed in the fine fraction. The fine dust samples were analyzed for PAH, nicotine, and cotinine.

#### INTRODUCTION

Recent studies have shown that significant levels of household pesticides occur in house dust.<sup>1</sup> Residues of the pesticides deposited on surfaces and contained in house dust or soil may be picked up by the skin on contact. Once on the skin, the pesticides may be absorbed directly or transferred to the mouth and ingested. Because small children spend a great deal of time on the floor, they are particularly susceptible to exposure to these compounds as a result of dermal contact with house dust and the frequent hand-to-mouth contact that accompanies their normal play activities.

Polynuclear aromatic hydrocarbons (PAH) and their derivatives represent another important group of semivolatile organic compounds (SVOC) that have been found in indoor air<sup>2,3,4</sup>. Although PAH have been identified in street dust samples,<sup>5</sup> little, if any, information is available about their occurrence and distribution in house dust. Many of these compounds are known to be carcinogenic or mutagenic to man, and a wide array of adverse health effects has been linked to exposure to

PAH.<sup>4,6</sup> The presence of environmental tobacco smoke (ETS) has been shown to be an important indoor source of PAH and PAH derivatives.<sup>2,3</sup>

Note that the particulate portion of ETS may accumulate onto the house dust and contribute to PAH levels in house dust. It is desirable to identify a suitable marker for particulate phase ETS in house dust. There are three potential markers for particulate phase ETS, nicotine, cotinine, and solanesol. Nicotine is a dominant component of ETS, and has been used as a marker for ETS, but it is primarily in the vapor phase.<sup>7</sup> Cotinine can be formed through oxidation of nicotine. Solanesol has been suggested to be a suitable marker for particulate-phase ETS, but this compound has also been reported to decompose under UV light, and under the temperatures of an automatic gas chromatography (GC) injector.<sup>8,9</sup> Studies are needed to investigate the analytical method for the determination of these potential ETS markers (nicotine, cotinine, and solanesol) in house dust samples, and to determine the storage stability of these compounds for selecting a suitable marker compound for ETS particles in house dust. In order to make an initial assessment of the relative importance of house dust to overall indoor exposure to PAH, a reliable analytical method is also needed to determine PAH and PAH derivatives in house dust.

In this paper we discuss the storage stability for the potential markers (solanosol, nicotine, and cotinine) for particulate-phase ETS in house dust, and the concentration profiles of PAH, nicotine, and cotinine in house dust samples from a small field study.

## EXPERIMENTAL PROCEDURE

### Storage Stability Study

In the storage stability study, eight aliquots (200 mg each) of a smoker's fine house dust particles ( $<150\ \mu\text{m}$ ) were used. Each of the four aliquots of house dust were spiked with a known amount of solanesol and each of the other four aliquots were spiked with a known amount of nicotine and cotinine. The spiked samples were stored at room temperature, under an indoor lighting environment for 0 day, 7 days, 14 days, and 21 days. The samples were then analyzed for solanesol, nicotine, and cotinine after the designated storage time. The analytical method used for the determination of solanesol consists of extracting the dust sample with dichloromethane (DCM), derivatizing the DCM extract with N,O-Bis(trimethylsilyl)trifluoroacetamide, and analyzing the sample extract by on-column injection, gas chromatography/flame ionization detection (GC/FID).<sup>10</sup> Analysis of nicotine and cotinine in house dust samples consists of extracting the dust sample with acidic water ( $\text{pH} = 1.2$ ), and analyzing the extracts by a Trace Atmospheric Gas Analyzer (TAGA) interfaced with a Battelle-developed non-aerosol vaporization device.<sup>10</sup> The analytical methods used to determine solanesol, nicotine, and cotinine in house dust were validated by determining recoveries of these target compounds in the spiked house dust samples.

### A Small Pilot Field Study

The study was performed at eight homes in Columbus, Ohio. Homes were selected on the basis of either the presence or absence of ETS in the home. Four homes with smokers and four homes with nonsmokers were included. The High Volume Small Surface Sampler (HVS3) was used to collect house dust samples.<sup>11</sup> The HVS3 unit was operated following the manufacturer's instructions,<sup>12</sup> and a draft ASTM standard method.<sup>13</sup> The sampling procedure was based on that followed in the House Dust/Infant Pesticides Exposure Study (HIPES). The collected dust samples were then sieved into coarse and fine ( $<150\ \mu\text{m}$ ) fractions. The fine fractions were used for subsequent analyses for PAH, cotinine, and nicotine. The analytical method for nicotine and cotinine described in the storage stability study cannot provide adequate detection sensitivity for

cotinine in the dust samples. Thus, an alternative method was used, consisting of extracting dust samples with DCM followed by methanol (MEOH), cleaning up the combined DCM and MEOH extracts by liquid-liquid partitioning, and analyzing the base fraction by GC/MS. Another aliquot of each dust sample was extracted with DCM, fractionated by a silica gel column, and analyzed by GC/MS to determine PAH.<sup>10</sup>

## RESULTS

The recovery data of solanesol spiked onto the smoker's and nonsmoker's house dust samples were 96 and 92 percent, respectively. This finding indicated that two sequential extractions with DCM for 20 min with an ultrasonic bath can quantitatively remove spiked solanesol from the house dust sample matrix. The recovery data of nicotine and cotinine from the spiked nonsmoker's house, using extraction with acidic water and analyzing by TAGA, were 100 and 65 percent, respectively. The alternative method consisting of extracting, liquid-liquid partitioning, and GC/MS analysis also provided quantitative recoveries of nicotine (100 percent) and cotinine (89 percent) from the spiked house dust sample. Quantitative recoveries of PAH were also obtained from the spiked house dust sample, and the recoveries ranged from 70 percent of cyclopenta[c,d]pyrene to 100 percent of phenanthrene.

In the storage stability study, we found that solanesol spiked onto dust samples was unstable and the recovery of the spiked solanesol was only 6.2 percent after 7 days of storage in a typical indoor environment (room temperature and indoor lighting). Thus, solanesol is not a suitable marker for the indication of aged particulate-phase ETS in house dust samples. Under the same storage conditions, the spiked nicotine decreased to about 30 percent of its original value after 21 days of storage, but the spiked cotinine was found to be stable after 21 days of storage. The above results suggested that cotinine is a suitable marker for ETS particles in house dust.

In the small pilot field study, most of the dust loading (69-85 percent) was found to be distributed in the fine fraction (<150  $\mu\text{m}$ ). Table 1 summarizes the measured nicotine and cotinine results for the fine dust samples. Higher concentrations of both nicotine and cotinine were found in fine dust samples from smokers' homes as compared to those from nonsmokers' homes. The highest levels of nicotine and cotinine were found in the smoker's home #H05DS and the lowest levels of nicotine and cotinine were found in the nonsmoker's home #H07DN. These findings were in agreement with the storage stability study results described before suggesting that cotinine is a good marker for ETS particles in house dust. Table 2 summarizes the PAH concentration data from the small pilot field study. The PAH concentrations ranged from 0.01 ppm (naphthalene) to 90 ppm (fluoranthene). Note that levels of most carcinogenic 5- and 6-ring PAH in dust are higher than those of most noncarcinogenic 2- and 3-ring PAH in dust. The known carcinogen benzo[a]pyrene (BaP) ranged in concentration from 1.8 - 53.8 ppm. The highest PAH concentrations were found in house dust samples from a nonsmoker's home (#H08DN). That house is within a quarter mile of a freeway and road construction was performed during the sampling period. These factors may have contributed to PAH levels. The levels of most PAH in home number H07DN also exceeded those in the smoker's homes. Therefore, the presence of ETS is not the only important factor to contribute to the PAH levels in house dust.

## CONCLUSIONS

The following conclusions can be drawn from this study:

1. Solanesol is not a suitable marker for aged ETS particles in house dust.

2. Higher levels of nicotine and cotinine were found in the smokers' homes as compared to nonsmokers' homes. However, cotinine appears to be a better marker than nicotine for aged ETS particles in house dust because cotinine is more stable than nicotine in the house dust matrix.
3. The presence of ETS is not the only significant factor to contribute to the PAH levels in house dust samples. Higher PAH levels were found in two nonsmokers' homes compared with house dust from all four smokers' homes.

#### DISCLAIMER

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Table 1. Nicotine and cotinine concentrations in fine house dust samples

House Code <sup>(a)</sup>	Concentration, ppm	
	Nicotine	Cotinine
H01DS	90	0.90
H02DN	5.5	0.31
H03DN	4.7	0.30
H04DS	44	5.1
H05DS	430	7.1
H06DS	140	1.5
H07DN	2.2	0.17
H08DN	3.6	0.20

- (a) In H01DS, H01 refers to the first house sampled, D refers to the dust sample, and S refers to a smoker's house. In H02DN, H02 refers to the second house sampled, D refers to the dust sample, and N refers to a nonsmoker's house.

Table 2. PAH concentrations in house dust samples

Compound	H01DS $\mu\text{g/g}^*$	H02DN $\mu\text{g/g}$	H03DN $\mu\text{g/g}$	H04DS $\mu\text{g/g}$	H05DS $\mu\text{g/g}$	H06DS $\mu\text{g/g}$	H07DN $\mu\text{g/g}$	H08DN $\mu\text{g/g}$
Naphthalene	0.01	0.16	0.09	0.24	< 0.01	0.23	0.06	0.35
Acenaphthylene	0.20	0.12	0.04	0.04	0.02	0.36	0.10	0.52
Acenaphthene	0.28	0.09	0.07	0.05	0.05	0.15	0.24	1.06
Fluorene	0.48	0.15	0.11	0.08	0.09	0.55	0.46	2.07
Phenanthrene	6.81	2.12	2.13	0.98	1.10	6.32	7.52	41.0
Anthracene	0.73	0.25	0.16	0.11	0.12	0.69	1.05	3.91
Retene	0.07	0.15	0.18	0.10	0.06	< 0.01	0.23	0.36
Fluoranthene	12.4	3.73	3.21	1.77	2.24	10.7	14.7	90.2
Pyrene	9.39	2.87	2.49	1.31	1.48	8.00	11.4	68.2
Benz(a)anthracene	3.31	1.29	1.04	0.48	0.70	4.08	5.07	24.4
Chrysene	5.71	2.18	1.61	1.00	1.14	6.15	7.17	34.4
Cyclopenta(c,d)pyrene	0.21	0.17	0.04	0.06	0.05	0.19	0.23	0.36
Benzofluoranthenes	10.06	3.70	3.52	1.64	2.56	5.64	15.4	103
Benzo(e)pyrene	3.60	1.65	1.60	0.70	0.25	2.40	6.58	40.7
Benzo(a)pyrene	12.7	21.1	1.80	11.0	3.94	1.97	7.71	53.8
Indeno(1,2,3-c,d)pyrene	5.52	2.71	1.79	1.27	0.91	4.09	6.86	40.8
Dibenzo(a,h)anthracene	1.81	0.96	0.67	0.37	0.21	1.83	2.10	7.49
Benzo(g,h,i)perylene	4.57	2.36	1.54	1.03	0.72	3.20	5.33	34.9
Coronene	2.15	1.43	0.70	0.50	0.21	2.05	1.89	7.22

\*  $\mu\text{g/g}$  = ppm

**SAMPLING, SUPERCRITICAL FLUID EXTRACTION (SFE) AND GC/MS ANALYSES OF INDOOR AIR SEMI-VOLATILE TOXIC ORGANICS**

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**ABSTRACT**

People spend most of their time within enclosed air spaces; in indoor environments most air pollutants are present in higher concentrations than in outdoor environments. Consequently, indoor air quality should be of greater concern with respect to respiratory exposure to harmful toxic substances.

Therefore, a method has been developed to sample indoor airborne carcinogenic polynuclear aromatic hydrocarbons (PAHs) in such a way to extract them by environmentally safe SFE with less sample handling.

**INTRODUCTION**

SFE offers cleaner extracts, less sample handling, and equivalent or better recoveries to conventional technologies. It is cost effective, time efficient and low in solvent waste generation.

But, supercritical CO<sub>2</sub> as such does not have the ability to quantitatively extract PAHs from most of the environmental matrices. Modifying the fluid might enhance the extraction efficiencies but the performance of the method is highly matrix-dependent<sup>1-3</sup>. Therefore, additional developmental work needs to be done.

This work describes method optimization for the extraction of PAHs from an environmental matrix, XAD-2 (styrene-divinylbenzene polymer) and also sampling indoor airborne PAHs on teflon impinged glass fibre filter and XAD-2 in such a way to extract them employing SFE.

**Experimental**

Sample preparation, extraction, and GC/MS analysis:

Spiking was done by injecting 0.500 mL toluene solution of PAHs standard into XAD-2. The samples were housed in a glass cylindrical cartridge (13 mm o.d.; 11 mm i.d.; 51 mm length. An indentation at the lower end of the cylinder provided a rim to support a 200/200 mesh stainless steel screen that held the sorbent bed. Atop the sorbent bed, a layer of glass wool and another similar screen were placed to hold it in place. After spiking, the solvent was allowed to evaporate on its own.

Extractions were done in a SFX 2-10 extractor with a 260D syringe pump (Isco, Inc., Lincoln, NE) employing SFC grade CO<sub>2</sub> (Airco Special Gases, Riverton, NJ). The sampling cartridge was inserted into a stainless steel cylindrical extraction module (without significant empty space) with an endcap and a filter element at the bottom. Prior to extraction a modifier (all HPLC grade solvents) was injected into the spiked XAD-2. Immediately, the upper endcap with a filter was placed onto the extraction module, hand tightened and the extraction sequence initiated. Initially the extraction was done with no flow of fluid (static extraction), which allowed the sample matrix to be steeped in the fluid and the added modifier. Dynamic extraction (i.e., with continuous flow of the fluid) was then conducted to collect the analytes. Flow rates were controlled (measured as liquid fluid at the pump) using 50 µm i.d. fused silica tubing as an outlet restrictor. The reported flow rate was computed by dividing the total volume of fluid used, by the duration of dynamic extraction. The extracts were collected by inserting the outlet end of the restrictor into a culture tube (13 mm i.d., 178 mm long) containing 6 mL methylene chloride. To avoid the cooling of the solvent caused by the expansion of the fluid, the collection system was kept in a bath of methanol. Because of high gas-flow (especially at higher fluid flow rates), there was considerable evaporation of methylene chloride. To compensate the loss, additional methylene chloride (nearly 12 mL) was added in batches into the collection tube to keep its volume always around 6 mL. The extracts were then concentrated to 0.5 mL under a stream of pure nitrogen at 45-50°C.

GC/MS analyses were performed, after adding d<sub>12</sub>-perylene as an internal

standard, with a Hewlett-Packard model 5890 GC equipped with a J&W DB-5 (60 m, 0.25 um film thickness, 250 um i.d.) column, a HP 5970 mass selective detector and a HP 7673A auto sampler. Selected ion monitoring mode quantitations were based on the integration of extracted ion chromatogram of the molecular ion of each PAH.

## **Results and Discussion**

### Optimizing SFE conditions:

#### Effect of modifier:

Of all the modifiers tested (methanol, 1-propanol, 2-methoxyethanol, acetone, chloroform, methylene chloride, toluene, chlorobenzene, acetonitrile, N,N-dimethylformamide), chlorobenzene showed the highest extraction efficiency of lower- as well as higher-molecular-weight PAHs. The energy barrier of desorption between the analyte and the adsorbent can be reduced by selective interaction of the aromatic ring in the modifier with the matrix-solute complex since XAD-2 also contains aromatic rings in its structure, as visualized by Pawliszyn et al<sup>1</sup>, which explains our result. But, the reason for chlorobenzene being better than even toluene might be due to very close polarity match between chlorobenzene and the PAHs. The polarity of the mobile phase mixture must be optimized to match that of the analyte(s) to attain maximum extractability<sup>5</sup>. Methylene chloride, the best solvent for PAHs, was not as good as chlorobenzene, which demonstrates that the extractability is governed by solute/matrix/fluid interactions, rather than by solute/fluid interactions.

The results shown in Table 1 indicate that the extractability is governed by concentration of the modifier too. A uniform increase in extraction efficiency was evident on progressively increasing the volume of chlorobenzene from 0.5 to 1.2 mL.

#### Effect of temperature and pressure:

The analyte has to diffuse out of the pores of the matrix into the carbon dioxide stream before being transported by the bulk fluid out of the extraction module into the collection vessel<sup>1</sup>, which could be achieved easily at high temperatures by decreasing the forces between the analyte and the matrix. In fact, use of high temperatures has rewarded (Table 1) possibly because the vapour pressures of analytes increase with temperature. Increasing the temperature from 50° to 200°C, with pure CO<sub>2</sub> extractions resulted in two-to six-fold increase in extraction efficiencies of PAHs from air particulate matter<sup>6</sup>. But, in our experiments increasing it beyond 100°C ended in either no effect at all, or decreased recoveries (Table 1). Probably decreasing the fluid density too much (at constant pressure) which happens on increasing the temperature, might reduce the fluid's solubilizing capacity.

Higher pressures like 450 atm were necessary for the complete recovery of the PAHs, especially the four and five ring PAHs from matrices like soil<sup>7</sup>. This is because raising the extraction pressure leads to higher fluid density which increases the solubility of the analytes. That is why, most of our extractions were done at 450 atm (Table 1-4).

#### Effect of extraction time and fluid flow rate fluid volume:

The recovery is affected most by extraction time and extraction pressure. The highest recoveries of PAHs from standard reference soil and marine sediment were achieved<sup>1</sup> at flow rates in excess of about 2 mL.min<sup>-1</sup> (as compressed fluid) and at 90°C. Therefore, simply by exposing the sample to more fluid by increasing the extraction flow rate, quantitative recoveries of PAHs from environmental matrices might be possible. However, increasing the flow rate to such a high level may make the analyte collection more difficult. Moreover, quantitative collection of relatively volatile analytes is convenient only with flow rates of up to at least 1 mL.min<sup>-1</sup>. Obviously, the alternative to maximize recovery is to lengthen the extraction time. The extraction of PAHs from a railroad bed soil showed virtually no dependence on the flow rate<sup>6</sup>, provided it is within 0.3-0.9 mL.min<sup>-1</sup>. To achieve highly efficient extractions, 3 to 5 void volumes of fluid must be flushed through the charged extraction vessel<sup>8</sup>.

As shown in Table 1-4, 65 min-long extraction flushing 4 to 5 void volumes of fluid through the charged extraction vessel helped us to accomplish efficient extractions. However, to validate our method two sequential extractions of the same sample was performed; the first fraction being collected during the first 65 min of dynamic extraction, following which the second fraction was collected

for further 25 min under the same extraction conditions as those employed for the first fraction; on analyzing the fractions separately, nothing was detected from each one of the second fractions of six replicate experiments (Table 3).

Because of unknown reasons, lengthening the static extraction time from 25 to 45 min and increasing the pressure from 450 to 475 atm caused reduction in recovery in most of the thirty PAHs spiked (Table 3, column # 1 versus # 3 values).

#### Effect of spiked amount and moisture content of the material:

The precision in the experimental technique includes the precision of the entire system involving the SFE, the off-line collection, and the GC/MS analysis. The precision became poor on reducing the spiked amount (Table 2).

As contemplated by Lopez-Avila et al<sup>1</sup>, a certain amount of water (10%) in the sample was observed to be beneficial (Table 4, data in column # 1 versus either # 2 or 3) especially in terms of extractability of higher-molecular-weight PAHs. The extractability of higher-molecular-weight PAHs was far better when 10% water was initially present in the matrix before the addition of the modifier (data in column # 2 versus # 3). Saturation of the solid matrix phase with the entrainers or modifiers like methanol and water, is crucial to obtain high recoveries of diuron from soil<sup>2</sup>; is the water modifying the solvent or modifying the matrix?

#### Sampling:

Sampling performed for continuous 24 h periods in a clean room indicated an absence of breakthrough of spiked compounds, but losses of some spiked compounds, attributed to reaction were detected (Table 4; data in column #4).

#### **CONCLUSION**

A method has been developed to sample, extract, and analyze indoor airborne PAHs.

#### **Acknowledgements**

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Table 1

Extraction Conditions<sup>a</sup>

	450 atm 100°C PhCl: 0.500 mL	450 atm 100°C PhCl: 1.000 mL	450 atm 100°C PhCl: 1.200 mL	450 atm 115°C PhCl: 1.000 mL	450 atm 115°C PhCl: 1.200 mL
	% Recovery				
	# 1	# 2	# 3	# 4	# 5
d <sub>10</sub> -Acenaphthene	69	74/7	93	73/0	73/4
d <sub>10</sub> -Anthracene	71	70/6	94	70/1	70/5
d <sub>10</sub> -Pyrene	64	70/6	94	73/2	69/8
d <sub>12</sub> -Chrysene	60	72/5	94	73/2	74/10
d <sub>12</sub> -Benzo[a]pyrene	54	68/5	83	68/6	71/9

<sup>a</sup> Supercritical fluid : CO<sub>2</sub>; modifier : PhCl; matrix : XAD-2 (1.5 g); volume of extraction cell (vertically kept) : 10 mL; volume of fluid employed : 52-67 mL; fluid flow rate : 0.59-0.78 mL.min<sup>-1</sup>; static : 15 min; dynamic : 86 min; amount spiked : 0.8005-0.8350 ug.

The values under the vertical column # 1 & 3 are from single determination while those under # 2 & 4 are from three determinations and those under # 5 are from two determinations.

Routine extractions at 115°C are impractical due to separation of extraction-cartridge's filter from its joint.

Table 2

Extraction Conditions<sup>a</sup>

		450 atm 100°C Static: 15 min Dynamic: 86 min	450 atm 100°C Static: 15 min Dynamic: 65 min	450 atm 100°C Static: 25 min Dynamic: 65 min
	Amount spiked (ug)	% Recovery <sup>b</sup>		
d <sub>10</sub> -Acenaphthene	0.8310	92.7 <sup>c</sup>	94.3/1.5	
d <sub>10</sub> -Anthracene	0.8010	93.6 <sup>c</sup>	89.2/2.3	
d <sub>10</sub> -Pyrene	0.8010	93.6 <sup>c</sup>	89.2/3.7	
d <sub>12</sub> -Chrysene	0.8005	93.7 <sup>c</sup>	82.3/4.7	
d <sub>12</sub> -Benzo[a]pyrene	0.8350	82.6 <sup>c</sup>	71.7/6.2	
Acenaphthene	0.2818			93.5/2.8
Anthracene	0.3082			83.9/5.1
Pyrene	0.4862			79.2/5.1
Chrysene	0.5025			76.0/5.0
Benzo[a]pyrene	0.6677			58.4/6.0

<sup>a</sup> Supercritical fluid : CO<sub>2</sub>; modifier : PhCl (1.200 mL); matrix : XAD-2 (1.5 g); volume of extraction cell (vertically kept) : 10 mL; volume of fluid employed : 37-66 mL; fluid flow rate : 0.57-0.99 mL.min<sup>-1</sup>.

<sup>b</sup> The numbers under the dividing bar represent standard deviations which are for six replicate extractions at each condition.

<sup>c</sup> These values are from only one extraction.

Table 3  
Extraction Conditions\*

	Amount spiked (ug)	450 atm	450 atm	475 atm
		100°C	100°C	100°C
		Static:	Static:	Static:
		25 min	30 min	45 min
		Dynamic:	Dynamic:	Dynamic:
		65 min	65 min	65 min
		% Recovery <sup>®</sup>		
		# 1	# 2	# 3
2-Methylnaphthalene	0.3305	104.9/5.1	97.3/4.7	85.3/5.6
1-Methylnaphthalene	0.3607	94.7/3.4	90.1/5.6	78.2/4.0
2-Chloronaphthalene	0.3237	97.8/4.1	94.8/2.8	127.9/6.4
Biphenyl	0.3105	100.9/4.3	98.2/2.1	114.0/7.5
Acenaphthalene	0.2597	90.5/1.9	84.1/4.7	94.7/3.4
Acenaphthene	0.2818	93.5/2.8	86.4/3.6	95.8/7.1
Fluorene	0.3325	94.7/3.5	89.7/3.7	92.6/5.5
Phenanthrene	0.3010	93.6/2.8	82.0/3.4	81.1/5.1
Anthracene	0.3082	83.9/5.1	81.7/3.8	74.6/5.2
o-Terphenyl	0.3252	96.3/1.4	87.1/2.1	93.5/5.2
1-Methylphenanthrene	0.4150	92.4/3.8	77.9/2.4	83.4/8.5
Fluoranthene	0.4165	86.0/3.7	75.2/4.0	71.0/5.6
Pyrene	0.4862	79.2/5.1	62.7/2.8	66.2/6.1
9,10-Dimethylanthracene	0.3987	34.3/46.5	76.9/10.0	62.2/24.9
m-Terphenyl	0.3082	93.0/5.8	82.8/3.2	83.7/7.0
p-Terphenyl	0.4050	93.0/4.7	93.4/9.3	74.6/3.5
Benzo[a]fluorene	0.6450	91.2/8.5	82.8/11.2	76.3/9.7
Benzo[b]fluorene	0.4060	77.2/9.9	70.2/4.5	72.4/6.1
Benz[a]anthracene	0.6435	71.7/7.9	57.8/3.5	55.3/5.7
Chrysene	0.5025	76.0/5.0	51.1/2.8	60.5/5.4
Benzo[b]fluoranthene	0.4030	78.6/19.6	51.7/6.4	43.2/6.3
Benzo[k]fluoranthene	0.4675	62.0/2.9	47.1/2.9	59.9/10.3
Benzo[e]pyrene	0.3752	56.4/7.6	42.2/5.0	34.1/1.7
Benzo[a]pyrene	0.6677	58.4/6.0	38.7/8.2	45.2/4.4
Perylene	0.3077	53.1/3.3	49.3/8.1	18.2/21.8
3-Methylcholanthrene	0.3850	55.9/11.3	0.0/0.0	46.2/5.6
Indeno[1,2,3-cd]pyrene	0.3457	28.0/18.6	33.8/12.9	38.8/6.0
Dibenz[ac/ah]anthracene	0.4185	41.4/14.1	33.1/13.9	44.4/7.4
Benzo[ghi]perylene	0.4722	44.8/5.3	32.1/12.4	45.3/11.2

\* Supercritical fluid : CO<sub>2</sub>; modifier : PhCl (1.200 mL); matrix : XAD-2 (1.5 g); volume of extraction cell (vertically kept) : 10 mL; volume of fluid employed : 37-59 mL; fluid flow rate : 0.57-0.90 mL.min<sup>-1</sup>.

® The numbers under the dividing bar represent standard deviations which are for five to six replicate extractions at each condition.

Column # 2 values represent the first fraction, collected during the first 65 min of dynamic extraction, following which a second fraction was collected for further 25 min in each one of the six replicate extractions under the same extraction conditions as those employed for the corresponding first fractions; on analyzing nothing was detected from each one of the second fractions.

Table 4

	Extraction Conditions <sup>a</sup>			
	475 atm 100°C Static: 45 min Dynamic: 65 min	475 atm 100°C Static: 45 min Dynamic: 65 min	475 atm 100°C Static: 45 min Dynamic: 65 min	450 atm 100°C Static: 25-45 min Dynamic: 65 min
	% Recovery <sup>b</sup>			
	# 1	# 2	# 3	# 4
2-Methylnaphthalene	85.3/5.6	85.6	87.6/2.8	>100/0
1-Methylnaphthalene	78.2/4.0	86.8	85.3/3.2	>100/0
2-Chloronaphthalene	127.9/6.4	80.3	80.4/3.1	>100/0
Biphenyl	114.0/7.5	88.6	87.1/2.5	>100/0
Acenaphthalene	94.7/3.4	89.7	88.1/1.2	50.1/5.1
Acenaphthene	95.8/7.1	86.6	86.7/3.0	92.5/9.6
Fluorene	92.6/5.5	82.4	80.2/2.3	76.2/6.7
Phenanthrene	81.1/5.1	85.4	86.1/3.7	78.6/3.0
Anthracene	74.6/5.2	81.8	84.3/3.2	0.0/0.0
o-Terphenyl	93.5/5.2	89.2	87.0/3.2	66.6/8.9
1-Methylphenanthrene	83.4/8.5	93.0	91.3/2.7	28.9/1.6
Fluoranthene	71.0/5.6	88.4	84.1/4.8	8.0/10.7
Pyrene	66.2/6.1	80.0	71.2/4.5	6.2/8.2
9,10-Dimethylanthracene	62.2/24.9	125.1	123.1/6.7	0.0/0.0
m-Terphenyl	83.7/7.0	91.2	89.6/3.2	0.0/0.0
p-Terphenyl	74.6/3.5	93.1	90.4/2.4	0.0/0.0
Benzo[a]fluorene	76.3/9.7	87.6	85.0/2.5	3.6/4.8
Benzo[b]fluorene	72.4/6.1	88.9	87.0/3.2	0.0/0.0
Benzo[a]anthracene	55.3/5.7	83.8	70.6/7.7	24.9/4.2
Chrysene	60.5/5.4	79.6	65.3/7.5	48.4/3.5
Benzo[b]fluoranthene	43.2/6.3	76.2	57.8/10.0	77.2/15.2
Benzo[k]fluoranthene	59.9/10.3	74.7	58.0/9.7	68.5/2.8
Benzo[e]pyrene	34.1/1.7	70.6	50.9/10.2	69.3/3.5
Benzo[a]pyrene	45.2/4.4	73.2	53.7/10.2	18.0/12.0
Perylene	18.2/21.8	67.9	47.7/12.1	21.7/14.4
3-Methylcholanthrene	46.2/5.6	81.6	64.7/10.3	0.0/0.0
Indeno[1,2,3-cd]pyrene	38.8/6.0	70.9	49.1/10.3	56.9/14.8
Dibenz[ac/ah]anthracene	44.4/7.4	70.0	49.4/10.0	42.2/16.5
Benz[ghi]perylene	45.3/11.2	62.7	42.1/9.6	69.2/6.1

<sup>a</sup> Supercritical fluid: CO<sub>2</sub>; modifier: PhCl (1.200 mL); matrix: XAD-2 (1.5 g); volume of extraction cell (vertically kept): 10 mL; volume of fluid employed: 40-60 mL; fluid flow rate: 0.60-0.90 mL.min<sup>-1</sup>; amount spiked: 0.2597-0.6677 ug.

<sup>b</sup> The numbers under the dividing bar represent standard deviations; the values under the vertical columns # 1 & 3 are from five replicate extractions at each condition while those under columns # 2 & 4 are from one and two determination(s) respectively; column # 1 values are from the set-up where no water was present with the matrix while column # 2 & 3 values are from the set-up where the matrix was made wet with 0.150 mL water, before extraction. However, column # 2 & 3 values differ in the respect that in # 2 case, water was injected in before the addition of chlorobenzene, while in # 3 case, the reverse addition was made; in these cases, the extract was dried with anhydrous sodium sulfate before analysis.

After spiking onto an teflon impinged glass fibre filter (47 mm diameter), at room temperature, clean air was pulled through it and two cartridges (one over the another, each carrying 1.5 g XAD-2) tightly securing the whole set-up in a milled aluminum housing, for 24 h; on extracting and analyzing each of the three components (one filter & two cartridges) individually (for the filter extraction, 2.5 mL extraction cell, 14.9-17.4 mL fluid and 0.23-0.27 mL.min<sup>-1</sup> flow rate was employed), nothing was detected from the bottom cartridge; column # 4 values represent total % recovery from the filter and the top cartridge.

**A DISCUSSION OF VOLATILE ORGANIC COMPOUND  
SAMPLING AND ANALYSIS USING A MOBILE GC/MS**

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**ABSTRACT**

To demonstrate the capability of a mobile gas chromatography/mass spectrometry unit to meet the criteria of volatile organic compound compliance testing, an experiment was conducted in two phases. Phase 1, conducted on March 4, 1993, involved tuning and calibrating the mobile unit according to OSW 846 Method 8240 specifications. For Phase 2, conducted on March 17, 1993, the mobile unit was moved to a different location. The instruments were retuned, continuing calibrations were performed, and laboratory and VOST audits were analyzed according to OSW 846 Method 5040A specifications. Overall, the system tuning, calibrations, and audit results, both laboratory and VOST, were determined to be successful. Since all requirements for compliance purposes were met during the demonstration, the mobile gas chromatography/mass spectrometry unit is capable of providing quality data in the field.

## INTRODUCTION

The need for quick turnaround multi-component emissions sampling and analysis precipitated the design and construction of a mobile gas chromatography/mass spectrometry (GC/MS) unit. The goal of this paper is to report the demonstrated success of performing on-site analysis of volatile organic compounds (VOCs) using a mobile GC/MS. The criteria met during this demonstration are compliance acceptable but can be used for field screening and engineering studies as well. Analyses were performed in accordance with the guidelines of OSW-846 Methods 8240 and 5040A.

Method 8240, based upon a purge-and-trap GC/MS procedure, is used to determine and quantify volatile organic compounds in solid waste matrices including ground water, sludges, liquors, solvents, oily wastes, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils, and sediments.

Method 5040A is used to determine and quantify gas stream volatile principal organic hazardous constituents (POHCs) collected on Tenax and Tenax/charcoal sorbent cartridges using a volatile organic sampling train (VOST). Because the majority of gas streams sampled using VOST contain a high concentration of water, the analytical method is based on the quantitative thermal desorption of volatile POHCs from the Tenax and Tenax/charcoal traps and analysis by purge-and-trap GC/MS.

Method 8240, which is referenced in Method 5040A, specifies the operating parameters and acceptance criteria for the GC/MS hardware. Method 5040A specifies the acceptance criteria for the GC/MS analytical procedures used in this demonstration.

## MOBILE GC/MS EQUIPMENT TECHNICAL INFORMATION

There were several important design needs that had to be met to ensure the integrity of the mobile unit. Some of these design needs included measures to reduce the risk of damage to the instrumentation during transport to the site and ensure the environment inside the mobile laboratory remains as contaminant-free as possible. Thus, these design needs led to the construction of a prototype air suspension table to isolate instrumentation from shock and vibration and state-of-the-art temperature controls operating during transport and while performing on-site analysis. Additionally, the mobile laboratory includes measures to avoid contamination such as high efficiency particle and hydrocarbon air filters and a forced air curtain to provide a barrier from air movement in or out of the mobile unit. Further, to ensure the mobile unit can operate independently, the mobile unit is equipped with two on-board 10 kVA diesel generators and an un-interruptable power supply (UPS) to provide battery backup. The system was designed such that the generators can be placed downwind from the mobile laboratory, ensuring no cross-contamination from the generators.

The mobile laboratory is equipped with an on-board VOST oven and Tekmar Model 2000 Purge and Trap and Hewlett Packard 5890-71A GC/MS able to quantitate compounds down to the 0.1  $\mu\text{g}$  level.

## THE DEMONSTRATION

The main objective of the demonstration was to perform analytical tuning and calibrations of the instrument, move it to another location, and then retune and check calibrations and recalibrate, if necessary. The secondary objective was to perform a full array of analytical procedures to demonstrate

acceptability compared to the guidance criteria in 8240 and/or 5040A. The demonstration was performed in two phases: Phase 1 was performed on March 4, 1993 and Phase 2 was performed on March 17, 1993. During each phase, the recommended GC/MS operating conditions listed in Table 1 were met.

The GC/MS was tuned and calibrated prior to analysis in accordance with 8240. Table 2 presents a summary of the analytical acceptance criteria for VOCs as specified in 8240. Each of the systematic criteria checks were performed with the mobile unit.

Table 1. Recommended GC/MS Operating Conditions - OSW 846 Method 8240

Electron Energy	70 volts
Mass range	35-260 amu
Scan time	1 sec/scan
Initial column temperature	45 °C
Initial column holding time	3 min
Column temperature program	8 °C/min
Final column temperature	220 °C
Final column holding time	15 min
Source temperature	According to manufacturer's specs
Transfer line temperature	250 °C
Carrier gas	Helium at 30 cm/sec

#### Phase 1 - March 4, 1993

On March 4, 1993 the instrument was installed in the truck and allowed time to equilibrate. Then an initial tuning and an initial calibration were performed.

##### The BFB Initial Tuning

The initial tuning involved introducing 50 ng of 4-bromofluorobenzene (BFB) standard as a reference compound to demonstrate that the GC/MS system was properly mass calibrated and tuned prior to performing the initial calibration. Specific mass spectral criteria must be met prior to performing initial or continuing calibrations. As shown in Table 3, the BFB key ions and abundance criteria were met. The time of starting the data acquisition for this analysis defines the beginning of the 12-hour clock for a valid set of analyses.

##### The Initial Calibration

The initial calibration was performed once the BFB tuning was demonstrated. The initial calibration involves the determination of a five-point calibration curve to demonstrate VOST purge and trap, GC, and MS (the system's) performance. An initial calibration was performed for the 8240 list of VOCs. The calibration solutions were spiked onto a Tenax/Tenax-Charcoal tube pair and then thermally desorbed through the purge and trap GC/MS system.

Table 2. Summary of Analytical Acceptance Criteria  
OSW-846 Method 8240/5040A

Quality Parameter	Method of Determination	Frequency	Criteria
Initial tuning	Hardware tuning using BFB	Prior to analyses; then every 12 hours	See Table 3.
Initial calibration	Five-point calibration curve	Prior to analyses; then mid-level check every 12 hours	< 30% RSD of average RF
System performance check	Determine RFs for system performance check compounds <sup>a</sup>	Prior to use of calibration curve; then every 12 hours	RF for each SPCC should be at least 0.30 except 0.25 for bromoform
Calibration check	Determine RFs for calibration check compounds <sup>b</sup>	After the SPC	<25 % deviation between initial RF and current RF
Consistency	Internal standard retention time and area from calibration check	Evaluate immediately after or during data acquisition	Retention time deviation of < 30 sec; EICP area deviation of less than a factor of 2
Accuracy	Spike each fraction with surrogates	Each fraction	50 - 150% recovery
Blanks	Method blank	One per set of samples	Less than lowest standard
	Field blank	One per test run series	Less than lowest standard

<sup>a</sup>Chloromethane, 1,1-dichloroethane, bromoform, 1,1,2,2-tetrachloroethane, chlorobenzene

<sup>b</sup>1,1-dichloroethene, chloroform, 1,2-dichloropropane, toluene, ethyl benzene, vinyl chloride.

Table 3. Initial Tuning Criteria  
BFB Key Ions and Abundance Criteria  
OSW 846 Method 8240

Mass	Ion Abundance Criteria	March 4, 1993	March 17, 1993
50	15 - 40% of mass 95	19.7	19.0
75	30 - 60% of mass 95	46.9	44.9
95	base peak, 100% relative abundance	100	100
96	5 - 9% of mass 95	8.3	8.2
173	< 2% of mass 174	0.0	0.0
174	> 50% of mass 95	81.7	91.6
175	5 - 9% of mass 174	5.5	8.2
176	> 95% but < 101% of mass 174	99.1	97.8
177	5 - 9% of mass 176	6.0	5.2

Included in the 8240 list were system performance check compounds (SPCC) (chloromethane, 1,1-dichloroethane, bromoform, 1,1,2,2-tetrachloroethane, and chlorobenzene), calibration check compounds (CCC) (1,1-dichloroethene, chloroform, 1,2-dichloropropane, toluene, ethylbenzene, and vinyl chloride), internal standards (bromochloromethane, 1,4-difluorobenzene, and chlorobenzene- $d_3$ ), and the surrogate standards (toluene- $d_8$ , 4-bromofluorobenzene, 1,2-dichloroethane- $d_4$ , benzene- $d_6$ , and o-xylene- $d_{10}$ ).

In accordance with Method 8240, the response factors (RF) for each compound relative to one of the internal standards were calculated at five concentration levels: 0.10  $\mu\text{g}$ , 0.25  $\mu\text{g}$ , 0.50  $\mu\text{g}$ , 0.75  $\mu\text{g}$ , 1.0  $\mu\text{g}$ . An average RF was calculated for each compound. An SPC was made before the calibration curves were used for analysis. The minimum acceptable average RF for volatile SPCCs is 0.30 for chloromethane, 1,1-dichloroethane, 1,1,2,2-tetrachloroethane, and chlorobenzene; for bromoform, the minimum acceptable average RF is 0.25.

As shown in Table 4, bromoform did not meet the 8240 minimum average response factor for the five calibration points. Bromoform is one of the compounds most likely to be purged very poorly if the purge flow is too slow. Cold spots and/or active sites in the transfer lines may adversely affect response.

The RFs from the initial calibration are used to calculate the percent relative standard deviation (%RSD) for calibration check compounds (CCCs). The %RSD for each individual CCC should be less than 30 percent. A CC is evaluated after the SPC is met. The CCCs are 1,1-dichloroethene, chloroform, 1,2-dichloropropane, toluene, ethylbenzene, and vinyl chloride and are used to check the validity of the initial calibration. As shown in Table 5, the % RSD for the initial calibration (ICAL) met the calibration criteria of less than 30 percent for all compounds.

#### Phase 2 - March 17, 1993

On March 17, 1993, the mobile GC/MS laboratory was moved to another location where the BFB initial tuning and continuing calibration (CONCAL) were performed. In addition, laboratory audits and VOST audit samples were analyzed.

##### The BFB Initial Tuning

Another BFB tuning was performed in accordance with Method 8240. Again, as shown in Table 3, the BFB key ions and abundance criteria were all within the acceptance criteria.

##### The Continuing Calibration

The initial calibration curve for each compound of interest must be checked and verified once every 12 hours of analysis time. This is known as a continuing calibration and is performed by analyzing a calibration standard that is at a concentration near the midpoint concentration for the working range of the GC/MS, which in this case was 0.25  $\mu\text{g}$ . The SPC acceptance criteria for the response factors are the same as for the ICAL: 0.30 minimum and 0.25 minimum for bromoform. Again, the bromoform was not within the acceptable range for Method 8240 (see Table 4).

Table 4. System Performance Check Compounds (SPCC)  
OSW Method 8240

Compound	Minimum Acceptable Average RF	March 4, 1993	March 17, 1993
		<u>ICAL</u> <u>RF</u>	<u>Concal</u> <u>RRF</u>
chloromethane	0.30	0.318	0.337
1,1-dichloroethane	0.30	2.24	2.25
bromoform	0.25	0.189*	0.183*
1,1,2,2-tetrachloroethane	0.30	0.520	0.516
chlorobenzene	0.30	0.891	0.921

\*Not accepted for Method 8240 (not required for Method 5040A)  
RF - response factor

Table 5. Calibration Check Compounds (CCC)  
OSW-846 Method 8240

Compound	% RSD Acceptance Criteria	ICAL % RSD	CONCAL %D
1,1 dichloroethane	< 30	6.95	0.3
chloroform	< 30	12.4	0.4
1,2-dichloropropane	< 30	3.91	12.6
toluene	< 30	6.31	4.5
ethyl benzene	< 30	2.27	9.9
vinyl chloride	< 30	15.21	8.2

After the SPC criteria are met, CC acceptance criteria are checked. The CC criteria are represented in terms of percent difference from the initial calibration to the continuing calibration. If the percent difference is less than 30%, then the continuing calibration is valid. In each case, the minimum acceptance criteria of the CC were met (see Table 5).

### Consistency

One of the analytical quality parameters to be determined is the consistency of the data. This is determined by the retention times and internal standard responses evaluated immediately after data acquisition of the samples. For purposes of discussion, the method and trip blanks, laboratory audits, and VOST sample audits are considered "samples." The compounds evaluated for this determination are the internal standards bromochloromethane, 1,4-difluorobenzene, and chlorobenzene- $d_5$ .

The criteria for the retention time are based on changes between the retention time measured in the sample and the retention time from the continuing calibration. If the retention time for any internal standard changes by more than 30 seconds, the chromatographic system must be inspected for malfunctions and corrections made. As shown in Table 6, each sample (Method Blank, Trip Blank, Lab Audit 1, Lab Audit 2, VOST sample Audit 1, and VOST sample Audit 2) are within the 30 second retention time criteria.

The criteria for the internal standard responses is based on changes between the area measured in the sample and the area measured for the continuing calibration. If the area for any of the internal standards changes by a factor of two (i.e., -50% to +100%), the mass spectrometer must be inspected for malfunctions and corrections made. As shown in Table 6, each sample was within the percent difference criteria.

### Accuracy

Another analytical quality parameter is the accuracy of the data. Accuracy is determined by the percent recovery of the surrogate compounds. These compounds included 1,2-dichloroethane- $d_4$ , benzene- $d_6$ , toluene- $d_8$ , o-xylene- $d_{10}$ , and bromofluorobenzene. A known amount, 0.25  $\mu\text{g}$ , of each surrogate was spiked into the samples. As shown in Table 7, the percent recovery criteria of 50 to 150% was met for each compound and sample with the exception of the VOST Audit 2 sample for BFB.

## AUDIT RESULTS

Two sets of audits samples were analyzed: (1) laboratory audits 1 and 2 and (2) the VOST sample audits, Audit 1 and Audit 2.

Laboratory Audits 1 and 2 each consisted of 10.8 liters of a National Institute of Standards and Technology (NIST) cylinder gas pulled directly onto one VOST Tenax tube. The purpose of these audits was to identify analytical error. The NIST cylinder gas was certified to one percent purity. The concentrations in the NIST cylinder gas ranged from 9.63 to 10.2 ppbvd per compound.

The VOST sample audits performed in the shop area purposely were not shielded from cross-contamination. The audits consisted of 10.618 liters for Audit 1 and 10.336 for Audit 2 of a NIST cylinder gas. The NIST cylinder gas was certified to one percent purity. The concentrations in the NIST gas cylinder ranged from 4.7 to 5.3 ppbvd per compound.

Table 6. Consistency Results

Retention Time Limit	Concal Standard	Method Blank		Trip Blank		Lab Audit 1		Lab Audit 2		VOST Audit 1		VOST Audit 2		Acceptance Criteria
		time	%D	time	%D	time	%D	time	%D	time	%D	time	%D	
bromochloromethane	13.31	13.31	-0.04	13.31	-0.03	13.32	-0.07	13.36	-0.29	13.36	-0.40	13.34	-0.26	+/- 0.5 min
1,4-difluorobenzene	16.63	16.64	-0.12	16.65	-0.15	16.67	-0.28	16.68	-0.37	16.68	-0.32	16.68	-0.34	+/- 0.5 min
chlorobenzene-d <sub>1</sub>	25.07	25.06	0.02	25.08	-0.03	25.11	-0.16	25.11	-0.19	25.11	-0.16	25.12	-0.96	+/- 0.5 min
Area Limit	Concal Standard	area	%D	area	%D	area	%D	area	%D	area	%D	area	%D	
bromochloromethane	23,893	24,956	-4.45	23,527	1.53	25,986	-8.76	21,340	10.69	21346	10.66	25,072	-4.93	-50 to +100%
1,4-difluorobenzene	101,925	115,245	-13.07	117,234	-15.02	118,716	-16.47	117,470	-15.25	112,621	-10.49	112,587	-10.46	-50 to +100%
chlorobenzene-d <sub>1</sub>	99,903	103,601	-3.70	88,743	11.17	109,424	-9.53	105,248	-5.35	103,818	-3.92	100,859	-0.96	-50 to +100%

Table 7. Accuracy Results

Compound	Spiked Amount (µg)	% RECOVERY						Acceptance Criteria Limits (%)
		Method Blank	Trip Blank	Lab Audit 1	Lab Audit 2	Sample VOST Audit 1	Sample VOST Audit 2	
1,2 dichloroethane-d <sub>4</sub>	0.25	98.00	108.49	105.50	114.95	113.90	104.93	50-150
benzene-d <sub>6</sub>	0.25	92.86	88.54	91.32	88.76	90.06	90.58	50-150
toluene-d <sub>8</sub>	0.25	105.84	116.85	101.87	100.76	103.68	103.35	50-150
o-xylene-d <sub>10</sub>	0.25	58.79	82.92	91.40	96.78	97.12	96.33	50-150
bromofluorobenzene	0.25	59.74	60.20	84.15	89.50	87.00	15.32 *	50-150

Table 8. Audit Results

Compound	Lab Audit 1	Lab Audit 2	VOST Sample Audit 1	VOST Sample Audit 2	Acceptance Criteria	Audit Pass			
						Laboratory		VOST	
						1	2	1	2
Vinyl chloride	23.8	34.9	75.2	56.2	50-150%	N*	N*	Y	Y
Trichlorofluoromethane	74.8	81.9	177	129	50-150%	Y	Y	N*	Y
Methylene chloride	83.3	99.9	229	213	50-150%	Y	Y	N*	N*
Chloroform	86.8	105	103	97.5	50-150%	Y	Y	Y	Y
1,2-Dichloroethane	108	132	128	122	50-150%	Y	Y	Y	Y
1,1,1-Trichloroethane	84.0	85.7	130	421	50-150%	Y	Y	Y	N*
Benzene	88.5	88.5	92.8	89.4	50-150%	Y	Y	Y	Y
Carbon tetrachloride	80.4	77.4	88.4	84.7	50-150%	Y	Y	Y	Y
1,2 Dichloropropane	80.8	76.6	64.2	74.2	50-150%	Y	Y	Y	Y
Trichloroethene	84.8	84.8	79.3	81.5	50-150%	Y	Y	Y	Y
Toluene	94.7	110	126	16,700	50-150%	Y	Y	Y	N*
Tetrachloroethane	96.0	97.5	95.6	166	50-150%	Y	Y	Y	N*
Chlorobenzene	81.3	87.9	68.4	78.6	50-150%	Y	Y	Y	Y
Ethylbenzene	89.8	89.8	77.2	84.0	50-150%	Y	Y	Y	Y
o-Xylene	79.9	82.2	72.6	78.9	50-150%	Y	Y	Y	Y

\*Did not meet minimum acceptance criteria.

The laboratory and VOST audits were performed independently, each using different cylinders, different sampling systems, and different technicians collecting the samples. Only the GC/MS instrument and operator were the same.

As shown in Table 8, the laboratory audits 1 and 2 failed for vinyl chloride; both VOST sample audits passed. Since the laboratory audit involved the use of one Tenax tube with no charcoal tube, the loss of vinyl chloride was probably due to poor retention of vinyl chloride on Tenax. All other compounds were within 50 to 150 percent recovery.

The VOST sample audits realized mixed results. Trichlorofluoromethane failed on Audit 1 and passed on Audit 2. Additionally, both laboratory audits passed, suggesting there was a sampling or sample recovery error. However, the VOST tubes used for the VOST audits had been taken to a facility which made trichlorofluoromethane, or freon-11; therefore, the tubes which were extras were probably contaminated in the field. Methylene chloride failed both VOST sample audits and passed both laboratory audits, again suggesting there was a sampling or sample recovery error. Methylene chloride is commonly used in the shop, possibly causing cross-contamination to the sampling train. The analyte 1,1,1-trichloroethane, tetrachloroethane, and toluene failed VOST sample Audit 2; the laboratory audit and VOST sample Audit 1 passed, suggesting a sampling or sample recovery error. Toluene, a common shop solvent, failed on the VOST sample Audit 2 at 16,700 percent recovery which was obviously cross-contamination.

## DISCUSSION AND CONCLUSION

The demonstration to show the capability of the mobile GC/MS unit to meet compliance criteria for VOC analysis had two objectives. The first objective, completed in two phases, was to tune and calibrate the instrument according to Method 8240 specifications, move the mobile unit to another location, retune, and recalibrate if necessary. The second objective was to demonstrate the acceptability of the analytical procedures for meeting VOC compliance requirements and was performed during Phase 2.

Phase 1 involved the BFB initial tuning and initial calibration which included a system performance check and a calibration check. The initial tuning and initial calibration criteria were met by all compounds except bromoform. Bromoform, which is not required by Method 5040A, did not meet the requirements of the SPC.

After the mobile unit was moved to another location, Phase 2 was initiated. This part of the demonstration involved retuning the instrument, checking the calibration, and analyzing the audit samples. The SPC and CC acceptance criteria for the continuing calibration is the same as for the initial calibration. Again, bromoform did not meet the Method 8240 specification for the SPC; however, the CC criteria were met. The first objective of the demonstration was considered a success.

During the analytical part of Phase 2, the consistency and accuracy of the data were determined by Method 8240 specifications. All of the data passed the consistency criteria for retention times and area counts. The accuracy criteria measured as percent recovery was met by all of the surrogates except bromofluorobenzene during VOST Audit 2. During the laboratory audit, all compounds except vinyl chloride, which is not usually a target analyte, passed. During the VOST audit, trichlorofluoromethane, methylene chloride, 1,1,1-trichloroethane, toluene, and tetrachloroethane failed at least one of the audits. Sampling and recovery contamination contributed to the failure of most of these compounds. Overall, the second objective was considered a success.

## References

1. OSW Method 8240 Gas Chromatography/Mass Spectrometry for Volatile Organics, September 1986.
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**METHOD 301 FIELD AND LABORATORY VALIDATION OF TARGET  
SEMI-VOLATILE ORGANIC COMPOUNDS USING SW-846 METHOD 0010**

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**ABSTRACT**

Laboratory and field validation experiments were devised for SW-846 Method 0010 at a non-recovery coke oven. A representative model was selected and sampling was conducted over a 72-hour period. Using Method 301 criteria, bias and precision calculations were determined for the target analytes: toluene, xylenes, (o-, m-, p-), phenol, cresol, naphthalene, and benzo-a-pyrene. Laboratory experimentation validated all analytes except toluene and naphthalene; field experiments validated SW-846 Method 0010 for all analytes. Since toluene and naphthalene are used as laboratory solvents, the laboratory validation results for these analytes were considered skewed due to contamination. SW-846 Method 0010 was judged validated by Method 301 specifications for representative sampling at non-recovery coke ovens.

**INTRODUCTION**

Non-recovery coke ovens utilize a coking technology which expends combustibles extracted from the coal as fuel for oxidation - producing heat, carbon dioxide, and water vapor. The finished product of the coking process is carbon, a raw material widely used in the steel industry. Because of this unique re-entrainment technique, non-recovery coke ovens use no other air emission control devices other than the precise monitoring and control of the coking process.

Because little data exist to characterize the emissions from this type of process, the U.S. Environmental Protection Agency (EPA), Office of Air Quality Planning and Standards (OAQPS), Emission Measurement Branch (EMB), in support of National Emission Standards for Hazardous Air Pollutants (NESHAPS) selected a representative model for the industry in order to develop a comprehensive source category document for the coke oven industry; in an effort to assess the potential environmental impact as directed by the Clean Air Act (CAA) of 1990, this database would serve as a standard from which to determine applicable emission limits.

Entropy Environmentalists, Inc. (Entropy) conducted a testing program to determine emissions from a non-recovery coke oven. The purposes of the three-day testing program were to provide a laboratory and field validation study of SW-846 Method 0010 [Modified Method Five (MMS)] and to perform an emissions characterization evaluation on the non-recovery coking process. Data collected should certify the use of Method 0010 sampling trains to characterize target semi-volatile organic compound emissions from non-recovery coke ovens. This paper addresses the results of the Method Validation Study.

### METHOD 301

Method 301, "Field Validation of Pollutant Measurement Methods From Various Waste Media," details procedures to be used when a test method is proposed to meet an EPA requirement in the absence of a validated method. The method includes procedures for determining and documenting the quality - defined as the systematic error (bias) and random error (precision) - of the measured concentrations of the source emissions.

In order to determine the bias and precision of a proposed sampling method, known concentrations of analytes or their surrogates are introduced to collection media and collocated, simultaneous samples are collected. By analyzing the recovery of the known, "spiked" compounds, any systematic positive or negative difference between measured and true values can be determined; these biases are commonly caused by interfering compounds in the effluent gas, calibration errors, and inefficient analyte collection. Calculated bias correction factors must fall within the 0.70 to 1.30 range specified by the protocol. By comparing the results of paired sampling trains, variability in data obtained from the entire measurement system (sampling and analysis) can be quantified. The precision of the proposed method must have a relative standard deviation  $\leq 50\%$  in order to be accepted as valid.

#### Validation Procedure

Because the semi-volatile organic analytes to be analyzed are quantified using gas chromatography/mass spectrometry (GC/MS), Method 301 specifies that isotopic spiking be used as the framework for this validation study. Sampling train media are spiked with surrogate compounds prior to field testing. Twelve samples are then collected for analysis using either paired or quadruplet collocated sampling trains. Paired, collocated sampling trains are defined as two probes arranged so that the probe tip is 2.5 cm from the outside edge of the second probe with a pitot tube on the outside of each. Sampling procedures outlined in detail in SW-846 Method 0010 are strictly followed, with the exception of the paired sampling train design and inclusion of surrogate compounds. Labeled isotope and/or deuterated mixtures are introduced at each phase of analysis to pinpoint sources of laboratory loss and thereby accurately determine the bias and precision of the proposed method.

#### Validation Calculations

Data obtained from the minimum of 12 runs (six pairs for collocated sampling trains) are utilized in the following calculations in order to derive the bias and relative standard deviation quantities and assess the significance of these values.

The sample mean uses the results from the analyses of the isotopically spiked field samples and is calculated using:

$$S_m = \frac{\sum_{i=1}^n x_i}{n} \quad (1)$$

where:

- $S_m$  = sample mean
- $x_i$  = ith measurement
- $n$  = sample size.

The bias is calculated using the sample mean and the value of the isotopically labeled

spike as follows:

$$B = S_m - CS \quad (2)$$

where:

B = bias  
S<sub>m</sub> = sample mean  
CS = amount spiked.

Next, the sample standard deviation is calculated using the following equation:

$$SD = \sqrt{\frac{\sum_{i=1}^n (X_i - S_m)^2}{n - 1}} \quad (3)$$

where:

SD = sample standard deviation  
x<sub>i</sub> = ith measurement  
S<sub>m</sub> = sample mean  
n = sample size.

The standard deviation of the mean is calculated by:

$$SDM = \frac{SD}{\sqrt{n}} \quad (4)$$

where:

SDM = standard deviation of the mean  
SD = sample standard deviation  
n = sample size.

The bias of the sample is tested for significance by calculating:

$$t = \frac{|B|}{SDM} \quad (5)$$

and comparing this result to the critical t-value for a two-sided test at the .05 level of significance, with n-1 degrees of freedom. If the calculated t-value is larger than t<sub>.025</sub>, the bias is considered significant and a correction factor must be calculated using the following:

$$CF = \frac{1}{1 + \frac{B}{CS}} = \frac{CS}{S_m} \quad (6)$$

$$0.70 \leq CF \leq 1.30 \text{ for validation}$$

where:

CF = correction factor

B = bias

CS = amount spiked

$S_m$  = sample mean

Finally, the precision, as measured by the percent relative standard deviation, is calculated by:

$$\%RSD = \frac{SD}{S_m} \times 100 \quad (7)$$

$$\%RSD \leq 50\% \text{ for validation}$$

where:

%RSD = percent relative standard deviation

SD = sample standard deviation

$S_m$  = sample mean.

### Sampling and Analytical Procedures

Method 0010 sampling was conducted over a 72-hour period on a non-recovery coke oven. Thirty-six ovens exhaust into four stacks via a common tunnel; therefore, each stack approximates the emission's flow rate of nine ovens combined. The coking process operates on a 48-hour staggered cycle that begins when the even numbered ovens are charged with approximately 40 tons of coal; oven heat extracts combustibles inherent in the coal and oxidizes them to produce more heat. Coal bakes in this manner for 48 hours, after which it is removed as the finished product coke. Twenty-four hours after charging the even numbered ovens, the odd numbered ovens are loaded with coal and begin the 48-hour cycle. The stack is a vertical duct with an inner diameter of 96 inches and two ports located 5.2 duct diameters from the nearest upstream disturbance and 0.82 diameters from the nearest downstream disturbance (stack exit). In compliance with EPA Method 1 criteria, 24 points were selected for isokinetic sampling; due to structural obstructions, only one port was employed and all 24 points were sampled along this single axis.

Because normal operating conditions offered the potential for varying emissions results, four testing conditions were arbitrarily defined. Condition I was isolated during the charging cycle; testing began at the beginning of the charge and continued three and a half hours into the charge for a total sampling time of two and a half hours. Condition II began where Condition I ended and was allotted six hours; with just enough down time for train turnarounds, actual sampling time was four hours. Conditions III and IV followed the same format as Condition II, including sampling and down time allotments.

Laboratory and field sample analyses were performed by Triangle Laboratories, Inc. (TLI) using the isotope spiking analytical protocol designed for the target analytes benzo-a-pyrene (BaP), cresol, naphthalene, phenol, toluene, and xylenes (o-, m-, p-).

Table 1 presents the relationship between each analyte and its respective surrogate and

internal standards. The six target analytes were analyzed versus their respective labeled internal standard; surrogate compounds were then quantitatively compared to the internal standards. By comparing the analytes and surrogates to the C1 internal standards, losses due to laboratory handling were corrected before calculations were performed. By comparing C1 compounds to their respective C3 internal standard, the validity of the analytical recovery was determined. Bias and relative standard deviation were then calculated from these measurements.

Table 1. Relationship of analytes, surrogates, and internal standards.

ANALYTE	SURROGATE SOLN C2	EXTRACTION INT STANDARD SOLN C1	ANALYSIS INT STANDARD SOLN C3
Toluene	Ethylbenzene-d <sub>10</sub>	Toluene d <sub>8</sub>	Dichlorobenzene-d <sub>4</sub>
Xylene	Ethylbenzene-d <sub>10</sub>	o-Xylene-d <sub>10</sub>	Dichlorobenzene-d <sub>4</sub>
Phenol	2-Chlorophenol-d <sub>4</sub>	Phenol-d <sub>5</sub>	Phenanthrene-d <sub>10</sub>
Cresol	2-Chlorophenol-d <sub>4</sub>	o-Cresol-d <sub>7H</sub>	Phenanthrene-d <sub>10</sub>
Naphthalene	Acenaphthene-d <sub>10</sub>	Naphthalene-d <sub>8</sub>	Chrysene-d <sub>12</sub>
Benz-a-pyrene	Benz-e-pyrene-d <sub>12</sub>	Benz-a-pyrene-d <sub>12</sub>	Perylene-d <sub>12</sub>
	Terphenyl-d <sub>14</sub>		

**Laboratory Validation.** The laboratory validation experiment was designed so that samples to be analyzed closely matched expected field sample concentrations for the analytes of interest. Front-half, back-half, and aqueous impinger fractions were created using the same reagents and rinses described in Entropy's test design; for continuity, analysis fractions followed the matrix employed by Entropy during field sampling and recovery, so that the "front-half" fraction included the filter and the probe rinse (methanol/methylene chloride), the "back-half" fraction included the XAD resin and the condenser rinse, and the "aqueous impinger" fraction included the reagent, moisture catch and rinse recovered from the sampling train impingers. The separate fractions were spiked with 50 µg of each analyte (ANALYTE) and surrogate (SOLN C2). XAD resin was also spiked with the pre-spike compound terphenyl-d<sub>14</sub>. Laboratory samples were prepared for extraction by fortifying each segment separately with 100 µg of deuterium-labeled compounds identical to the analytes of interest, excluding the isotopic label (SOLN C1); extractions were performed and evaporated to 5 mL. Prior to GC/MS analysis, the three extracted constituents were separately fortified with a second set of deuterium-labeled compounds (SOLN C3) as internal recovery standards and a 10 mL aliquot was sampled for analysis.

Using a pre-determined mass for each compound to generate selected ion current profiles for quantification, each compound was measured against its respective standard. Analyte and surrogate recoveries were compared against C1 internal standards and C1 solutions were compared against C3 internal standards. These comparisons allowed TLI to correct for analyte or surrogate losses due to laboratory handling. In the same manner, pre-spiked terphenyl-d<sub>14</sub> and laboratory spiked standards recovery were quantified relative to the recovery internal standards.

**Field Validation.** The field validation procedure involved pre-spiking the XAD resin for all samples prior to field sampling. Isotopically labeled compounds were selected as surrogates for the targeted analytes because these compounds were chemically analogous to the compounds of interest. The relationship between the analytes and the surrogates is shown in Table 1. XAD resin was pre-spiked with the surrogate solutions and terphenyl-d<sub>14</sub> by directly introducing 50 µg of each compound in a methylene chloride solution via a syringe into the inlet end of the XAD trap before sealing and packing the traps for shipping to the test site. Recovery of the surrogate compounds was intended to demonstrate the ability of the entire methodology to achieve the Method 301 criteria.

Field samples were prepared for extraction by fortifying each fraction (front-half, back-half, and impingers) separately with 50 µg each of deuterium-labeled internal standards (SOLN C1), compounds that are identical to the analytes of interest excluding the isotopic label. The target analytes were measured versus these internal standards and any loss due to laboratory handling was corrected during the analytical calculations.

Prior to GC/MS analysis, the separate fractions were fortified with the deuterium-labeled recovery standards (SOLN C3) listed in Table 1. Internal standards recoveries were measured relative to these recovery standards.

Method 301 specifies that paired trains be used; however, the validation calculations given do not pair the data. Therefore, the bias and percent relative standard deviation verifications required by Method 301 were determined two ways: (1) using valid paired train data only and (2) using all valid data, excluding field blanks. Results were then compared to see if different conclusions would be reached. There were 14 measurements or seven pairs of data for all surrogates except 2-chlorophenol-d<sub>4</sub>, for which there were 12 measurements or six pairs of data.

All sample concentrations were given in micrograms (µg) using Equation (8):

$$\text{Amount, } \mu\text{g} = \frac{\text{Area X} \times \text{Amt Int Std} \times \text{Dilution Factor}}{\text{Area Int Std} \times \text{RF X}} \quad (8)$$

where:

- X = Analyte
- Int Std = Internal Standard
- Amt Int St = Amount Internal Standard = 50 µg
- RF X = Response Factor of Analyte X from following Calibration Point

## RESULTS

### Laboratory Validation

Method 301 does not address the question of whether to correct the data for blanks before proceeding with the validation protocol. Therefore, for comparison, analyte and surrogate results are reported both with and without blank correction. Method 301 specifies that 12 samples be analyzed; however, because the validation would be determined under a laboratory control, only three samples were spiked and analyzed. Since the three fractions were spiked with the analytes, as well as the surrogates, direct validation of both analytes and surrogates was possible. Therefore, the reported analyte results were not determined by the corresponding surrogate results. The results of the laboratory validation are presented in Tables 2, 3, and 4.

**Front-half Analyses.** Without blank correction, all of the analytes and C2 surrogates passed the validation requirements (see Table 2). The %RSD's ranged from 1.88% to 6.43%. The analytes toluene, and BaP, as well as the surrogates 2-chlorophenol-d<sub>4</sub> and benz-e-pyrene-d<sub>12</sub>, required calculation of correction factors of 0.81, 1.30, 1.17, and 1.15, respectively.

With blank correction of the data, the %RSD's ranged from 1.88% to 7.25%, all meeting the requirement of less than 50%. 2-chlorophenol-d<sub>4</sub>, benzo-e-pyrene-d<sub>12</sub>, and benzo-a-pyrene required correction factors which were 1.17, 1.15, and 1.46, respectively. Thus, BaP failed Method 301, which specifies that correction factors fall within 0.7 to 1.30, inclusive.

**Back-half Analyses.** Naphthalene failed validation without a blank correction, having a %RSD of 53.56% (see Table 3). The other %RSD's ranged from 1.43% to 9.11%. Toluene also failed validation with a correction factor of 0.61.

With blank correction, naphthalene still failed with a %RSD of 58.86%, which is higher than when the data are uncorrected. However, toluene now meets both the precision and bias requirements. This is not surprising since naphthalene is a common contaminant of the XAD resin and toluene is omnipresent in a laboratory environment. The other target compounds meet Method 301 criteria.

**Impinger Analyses.** Without blank correction, all analytes and C2 surrogates analyzed for the impinger fraction pass the %RSD requirement, with values ranging from 0.73% to 25.36% (see Table 4). Toluene and benzo-e-pyrene-d<sub>12</sub> both failed validation because of their bias correction factors of 0.27 and 1.31, respectively.

With blank correction, toluene still failed validation with an absolute %RSD of 109.21%. The adjusted correction factor for benz-e-pyrene-d<sub>12</sub> remained 1.31, just outside the range specified in Method 301.

### **Field Validation**

In order to apply EPA Method 301 procedures for validation, the amounts ( $\mu\text{g}$ ) of spiked surrogates that were recovered were calculated based on the corrected percent recovery and the amount of labeled compounds spiked (50  $\mu\text{g}$ ). The validation protocol specifies that paired trains be used for the isotope spiking procedure. However, the bias and precision calculations do not involve the use of paired data. Therefore, the method validation procedures were followed using paired and unpaired data in order to compare results. The results of the field validation are presented in Tables 5 and 6.

**Paired Train Results.** The paired train calculations validated Method 0010 for the field experiment (see Table 5). The %RSD's for the surrogates ranged from 5.56% to 36.86%. Therefore, the method met the precision requirement for each surrogate as specified by Method 301. Two surrogates, ethylbenzene-d<sub>10</sub> and 2-chlorophenol-d<sub>4</sub>, required bias correction factors. These correction factors were 0.798 and 0.889, respectively; therefore, the bias requirement was met by all surrogates as specified by the method. Since the spiked surrogates were chosen because they are chemically similar to the analytes of interest and since all surrogates passed validation, all of the analytes passed validation in the field.

Table 2. Laboratory validation results - front-half fraction.

FRONT-HALF UNCORRECTED	PRECISION		BIAS	
	%RSD	PASS/FAIL	CORRECTION FACTOR	PASS/FAIL
<b>ANALYTE</b>				
toluene	5.57	Pass	0.81	Pass
xylene	6.38	Pass	NA	Pass
phenol	5.57	Pass	NA	Pass
cresol	5.16	Pass	NA	Pass
naphthalene	5.70	Pass	NA	Pass
benzo-a-pyrene	6.43	Pass	1.30	Pass
<b>SURROGATE</b>				
ethylbenzene-d <sub>10</sub>	1.88	Pass	NA	Pass
2-chlorophenol-d <sub>4</sub>	2.55	Pass	1.17	Pass
acenaphthene-d <sub>10</sub>	2.93	Pass	NA	Pass
benzo-c-pyrene-d <sub>12</sub>	2.32	Pass	1.15	Pass
<b>FRONT-HALF CORRECTED</b>				
<b>ANALYTE</b>				
toluene	6.68	Pass	NA	Pass
xylene	6.36	Pass	NA	Pass
phenol	5.60	Pass	NA	Pass
cresol	5.14	Pass	NA	Pass
naphthalene	5.70	Pass	NA	Pass
benzo-a-pyrene	7.25	Pass	1.46	Fail
<b>SURROGATE</b>				
ethylbenzene-d <sub>10</sub>	1.88	Pass	NA	Pass
2-chlorophenol-d <sub>4</sub>	2.56	Pass	1.17	Pass
acenaphthene-d <sub>10</sub>	2.93	Pass	NA	Pass
benzo-c-pyrene-d <sub>12</sub>	2.32	Pass	1.15	Pass

Table 3. Laboratory validation results - back-half fraction.

BACK-HALF UNCORRECTED	PRECISION		BIAS	
	%RSD	PASS/FAIL	CORRECTION FACTOR	PASS/FAIL
<b>ANALYTE</b>				
toluene	9.11	Pass	0.61	Fail
xylene	2.63	Pass	NA	Pass
phenol	2.25	Pass	NA	Pass
cresol	6.63	Pass	NA	Pass
naphthalene	53.56	Fail	NA	Pass
benzo-a-pyrene	2.13	Pass	1.25	Pass
<b>SURROGATE</b>				
ethylbenzene-d <sub>10</sub>	4.19	Pass	NA	Pass
2-chlorophenol-d <sub>4</sub>	1.43	Pass	1.19	Pass
acenaphthene-d <sub>10</sub>	3.08	Pass	NA	Pass
benzo-e-pyrene-d <sub>12</sub>	2.73	Pass	1.12	Pass
<b>BACK-HALF CORRECTED</b>				
<b>ANALYTE</b>				
toluene	16.30	Pass	NA	Pass
xylene	2.63	Pass	NA	Pass
phenol	2.27	Pass	NA	Pass
cresol	6.61	Pass	NA	Pass
naphthalene	58.86	Fail	NA	Pass
benzo-a-pyrene	2.16	Pass	1.25	Pass
<b>SURROGATE</b>				
ethylbenzene-d <sub>10</sub>	4.18	Pass	NA	Pass
2-chlorophenol-d <sub>4</sub>	1.45	Pass	1.19	Pass
acenaphthene-d <sub>10</sub>	3.10	Pass	NA	Pass
benzo-e-pyrene-d <sub>12</sub>	2.68	Pass	1.12	Pass

Table 4. Laboratory validation results - impinger fraction.

IMPINGERS UNCORRECTED	PRECISION		BIAS	
	%RSD	PASS/FAIL	CORRECTION FACTOR	PASS/FAIL
<b>ANALYTE</b>				
toluene	25.36	Pass	0.27	Fail
xylene	3.02	Pass	NA	Pass
phenol	1.75	Pass	NA	Pass
cresol	2.88	Pass	NA	Pass
naphthalene	9.59	Pass	NA	Pass
benzo-a-pyrene	1.62	Pass	1.26	Pass
<b>SURROGATE</b>				
ethylbenzene-d <sub>10</sub>	4.92	Pass	NA	Pass
2-chlorophenol-d <sub>4</sub>	0.73	Pass	0.77	Pass
acenaphthene-d <sub>10</sub>	2.45	Pass	NA	Pass
benzo-e-pyrene-d <sub>12</sub>	5.60	Pass	1.31	Fail
<b>IMPINGERS CORRECTED</b>				
<b>ANALYTE</b>				
toluene	-109.21	Fail	NA	Pass
xylene	2.99	Pass	NA	Pass
phenol	1.74	Pass	NA	Pass
cresol	2.86	Pass	NA	Pass
naphthalene	9.59	Pass	NA	Pass
benzo-a-pyrene	1.60	Pass	1.26	Pass
<b>SURROGATE</b>				
ethylbenzene-d <sub>10</sub>	4.93	Pass	NA	Pass
2-chlorophenol-d <sub>4</sub>	0.71	Pass	0.77	Pass
acenaphthene-d <sub>10</sub>	2.44	Pass	NA	Pass
benzo-e-pyrene-d <sub>12</sub>	5.65	Pass	1.31	Fail

Table 5. Field Validation Results - Paired Data.

SURROGATE	ANALYTE	PRECISION		BIAS	
		%RSD	PASS/FAIL	CORRECTION FACTOR	PASS/FAIL
ethylbenzene-d <sub>10</sub>	toluene, xylene	5.56	Pass	0.798	Pass
2-chlorophenol-d <sub>4</sub>	phenol, cresol	6.00	Pass	0.889	Pass
acenaphthene-d <sub>10</sub>	naphthalene	29.30	Pass	NA	Pass
benzo-e-pyrene-d <sub>12</sub>	benzo-a-pyrene	36.86	Pass	NA	Pass

**Unpaired Train Results.** The same validation procedures were followed using all the data that were followed using paired train data; validation was again supported by the results (see Table 6). The same two surrogates, ethylbenzene-d<sub>10</sub> and 2-chlorophenol-d<sub>4</sub>, were found to have significant biases with corresponding correction factors of 0.82 and 0.91, respectively, which fall within the specified range of 0.7 to 1.3. The %RSD's for all surrogates ranged from 6.79% to 33.26%, all less than the 50% requirement. Therefore, all analytes passed the field validation according to Method 301.

Table 6. Field Validation Results - Unpaired Data.

SURROGATE	ANALYTE	PRECISION		BIAS	
		%RSD	PASS/FAIL	CORRECTION FACTOR	PASS/FAIL
ethylbenzene-d <sub>10</sub>	toluene, xylene	6.79	Pass	0.815	Pass
2-chlorophenol-d <sub>4</sub>	phenol, cresol	7.69	Pass	0.906	Pass
acenaphthene-d <sub>10</sub>	naphthalene	29.19	Pass	NA	Pass
benzo-e-pyrene-d <sub>12</sub>	benzo-a-pyrene	33.26	Pass	NA	Pass

## CONCLUSIONS

### Laboratory Validation

Method 301 specifies that isotope spiking may be performed in field validation procedures. However, it does not address the use of analyte vs. surrogate in the laboratory. Since both analytes and surrogates were spiked during the laboratory validation, the opportunity arose to directly compare analyte and surrogate results.

The method was judged successful without qualification for the analytes xylene, phenol, and cresol, along with their corresponding surrogates ethylbenzene-d<sub>10</sub> and 2-chlorophenol-d<sub>4</sub>. However, differences were found between benzo-a-pyrene and its corresponding surrogate benzo-e-pyrene-d<sub>12</sub> in the separate fractions analyzed. Discrepancies between BaP and its surrogate BeP-d<sub>12</sub> suggest that some interference may have been occurring during the GC/MS analyses. Since the two correction factors were very close to one another (a difference of 0.05) and the correction factor for BeP-d<sub>12</sub> fell just outside the interval [0.70, 1.30], it appears that BeP-d<sub>12</sub> is an appropriate surrogate for BaP and that BeP-d<sub>12</sub> may be considered to have passed validation.

Toluene failed validation completely in the impingers, while naphthalene failed validation completely in the back-half. Anticipated background contamination made naphthalene and toluene analyses results unreliable and inconclusive. XAD resin inherently contains naphthalene which is difficult to completely remove. Toluene is commonly used as an extraction solvent in laboratories. Every effort was made to reduce all laboratory evaluation samples and instrumentation exposure to toluene; however, this was judged by TLI to have been only moderately successful. This contamination may explain why the surrogates ethylbenzene-d<sub>10</sub> and acenaphthene-d<sub>10</sub> unconditionally passed validation in all three fractions, while their corresponding analytes, toluene and naphthalene, did not completely pass validation in the laboratory.

### **Field Validation**

The field validation was approached two ways: (1) using paired data, as per the protocol and (2) using unpaired data. This approach was taken since the bias and precision calculations do not involve the use of paired data. In both cases, validation was achieved for all surrogate compounds, and therefore, for all analytes. The precision of only two compounds was lower using the paired data; the precision of the other three compounds was higher. The biases of the compounds were essentially the same between the paired and single data.

The field validation procedures only involved analyzing the XAD for the surrogates since the XAD was the only fraction that was prespiked with the surrogate compounds. However, in the laboratory, all three fractions were spiked with the C2 compounds and the analytes. The variability in the recovery of these compounds from the front-half and the impingers, as well as the XAD, demonstrates the need for separate extractions and analyses of the various fractions. Additionally, the recoveries of labeled compounds spiked prior to extraction were variable. This variability, especially between dual trains, suggests that further research on this subject is necessary and that dynamic spiking may be needed.

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## HYDROCARBONS IN THE RANGE OF C10-C20 EMITTED FROM MOTOR VEHICLES; DIESEL VERSUS SPARK IGNITION

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### ABSTRACT

To understand better the sources of observed differences between on-road vehicle emissions and model estimates, a series of experiments was conducted in the Fort McHenry Tunnel, Baltimore, Maryland (June 18-24, 1992). It is a four-bore tunnel, two lanes per bore, carrying the eight lanes of Interstate 95 east-west under the Baltimore Harbor. Since heavy-duty trucks are directed into the right-hand bore, sampling in both right- and left-hand bores permitted an assessment of the relative importance of light-duty (mostly gasoline) versus heavy-duty (mostly diesel) vehicle emissions.

Samples were collected using stainless steel canisters (whole air samples, analyzed for C2-C12 hydrocarbons) and Tenax-TA solid adsorbent cartridges (for semi-volatile hydrocarbons, in the range C8-C20). The samples were analyzed using high resolution gas chromatographic separation and Fourier transform infrared/mass spectrometric detection (GC/IRD/MSD) or flame ionization detection (GC/FID). Comparison of hydrocarbon concentrations found in the Tenax and canister samples collected in the right- and left-hand bores of the Tunnel enables an assessment of the contribution of semi-volatile hydrocarbons (C10-C20 range derived from Tenax data) to the total non-methane hydrocarbons (C2-C20, derived from canisters and Tenax data).

### INTRODUCTION

Motor vehicles are a leading (and possibly the major) source of VOC and NO<sub>x</sub>, the precursors of ozone formation in urban areas throughout the United States. Yet, current motor vehicle VOC emissions estimates are low, by a factor of two to four (Ingalls, 1989<sup>1</sup>; Ingalls et al., 1989<sup>2</sup>; Fujita et al., 1992<sup>3</sup>). The reason for the discrepancy is under debate, but generally it is a difference between real-world vehicles, including the way they are maintained and driven, and estimates based on dynamometer measurements of volunteer fleets. To provide reliable real-world emission data for mobile sources, comprehensive monitoring was carried out in a highway tunnel (Fort McHenry Tunnel, Baltimore, Maryland). The overall objective of the Tunnel Experiment was to procure accurate data on motor vehicle emissions of carbon monoxide (CO), oxides of nitrogen (NO<sub>x</sub>), and volatile organic compounds (VOC) throughout the U.S. One of the specific objectives was to assess the relative importance of light-duty spark ignition vehicle emissions versus the heavy-duty diesel (HDD) emissions. It has been shown, for ambient air samples collected in a heavily traveled mountain tunnel with a high percentage of HDD traffic, that n-alkanes up to C26 could be detected in the gas-phase samples (Hampton et al., 1982<sup>4</sup>; 1983<sup>5</sup>). Thus, it was important to assess the contribution of hydrocarbons ranging from C10 to C20 (or higher), so-called semi-volatile hydrocarbons (SVHC), to total non-methane hydrocarbons (TNMHC) emitted from diesel vehicles. It has been reported (Zielinska and Fung, 1992<sup>6</sup>; 1993<sup>7</sup>) that this contribution is rather low for highway tunnel traffic dominated by light-duty spark ignition vehicles. The traffic from HDD vehicles in the Fort McHenry Tunnel, selected for the present study, was relatively high. In addition, since heavy-duty trucks were directed into the right-hand bore, sampling in both right- and left-hand bores permitted an assessment of the relative importance of emissions from light-duty (mostly gasoline) versus heavy-duty (mostly diesel) vehicles.

### EXPERIMENTAL METHODS

#### Sampling

The Fort McHenry Tunnel, located in Baltimore, Maryland, is the world's largest underwater tunnel designed for motor vehicle traffic. It is a four-bore tunnel, two lanes per bore, carrying the eight lanes of Interstate 95 east-west under the Baltimore Harbor. Its length is 2,195 m from portal to portal westbound, and 2,174 m eastbound. The downgrade in the tunnel reaches -3.76% and the upgrade reaches +3.76%, for both eastbound and westbound traffic. The Bores #1 and #2 are westbound (towards Washington, DC) and #3 and #4 are eastbound (toward the northeast). The sampling was performed in Bores #3 (light-duty vehicles only) and #4 (light- and

heavy-duty vehicles). The sampling sites were located in the west (entrance) and east (exit) portals in the overhead exhaust ducts of both bores, and in midtunnel beneath the roadway, in order to separate the downhill from uphill sections of the tunnel. In addition, ventilation air, supplied from entrance and exit buildings was also sampled. The five measurement stations per bore resulted in 10 canister and 10 Tenax samples per run. Sampling consisted of 11 one-hour runs during the period June 18-24, 1992. Each run was triggered by traffic count and composition (see Figure 1). Whole air samples, analyzed for C2-C12 hydrocarbons, were collected using the stainless steel canister sampling method. Semi-volatile hydrocarbons, in the range of C8-C20, were collected using Tenax-TA solid adsorbent. The canister and Tenax samplers were located side by side in the ventilation ducts of the tunnel, with Teflon sampling lines extending from the samplers through the ventilation louvers into the tunnel area. The Tenax sampling unit drew two parallel streams of air (at ~0.5 L/min and ~0.7 L/min per stream). Prior to use, the Tenax-TA solid adsorbent was cleaned by Soxhlet extraction and thermally conditioned for four hours by heating at 280 °C under nitrogen purge. Approximately 10% of the precleaned Tenax cartridges were tested by GC/FID for purity prior to sampling. After sampling, the Tenax cartridges were capped and placed in tin containers with activated charcoal on the bottom, and kept on ice until transported to a laboratory freezer.

Stainless steel Summa-polished canisters of 6 L capacity, employed for volatile hydrocarbon (C2-C12) collection, were cleaned by repeated evacuation and pressurization with humidified zero air prior to sampling, and certified as described by U.S. EPA Method TO-14<sup>8</sup>. The sampling procedure essentially followed the pressurized sampling method described by EPA Method TO-14.

#### Analysis

Tenax samples were analyzed by the thermal desorption-cryogenic preconcentration method, followed by high resolution gas chromatographic separation and Fourier transform infrared/mass spectrometric detection (GC/IRD/MSD; Hewlett Packard 5890 II GC with 5979 MSD and 5965B IRD) or flame ionization detection (FID) of individual hydrocarbons. The Chrompack Thermal Desorption-Cold Trap Injection (TCT) unit, which can be attached to either the GC/FID or the GC/IRD/MSD system, was used for sample desorption and cryogenic preconcentration. A 60 m (0.32 id, 0.25 µm film thickness) DB-1 capillary column (J&W Scientific, Inc.) was used and the chromatographic conditions were as follows: initial column temperature of 30 °C for two minutes, followed by programming at 6 °C/min to a final temperature of 290 °C and held isothermal for five minutes. Several Tenax cartridges from each sampling period and sampling location were analyzed by the GC/IRD/MSD technique in order to identify individual hydrocarbons. Identification of individual components was made based on their retention times and mass and infrared spectra matching those of authentic standards. If authentic standards were not available, the National Institute of Standards and Technology (NIST) mass spectral library (containing over 43,000 mass spectra) and the U.S. EPA infrared spectra library were used for compound identification. The quantification of hydrocarbons collected on all remaining Tenax cartridges was accomplished by the GC/FID technique. For calibration of the GC/FID, a set of standard Tenax cartridges was prepared by spiking the cartridges with a methanol solution of standard SVHC, prepared from high-purity commercially available C9-C18 aliphatic and aromatic hydrocarbons (Alltech Associates, Inc.). Ethylbenzene, 1,3,5-trimethylbenzene, n-dodecane, and n-tetradecane were used in the concentration range from ~7-8 ng/Tenax up to 200-300 ng/Tenax. The solvent was then removed with a stream of N<sub>2</sub> (5 min, 100 ml/min at room temperature) and the Tenax cartridges were thermally desorbed into the GC system, as described above. At least four concentrations of standard compounds were employed. Area response factors per nanogram of compound were calculated for each concentration and each hydrocarbon and then the response factors were averaged to give one factor for all hydrocarbons measured.

The stainless steel canister samples were analyzed for volatile (< C12) hydrocarbons using high resolution capillary gas chromatography with flame ionization detector (Hewlett-Packard 5890 Series II), after cryogenic sample concentration in a freeze-out loop made from chromatographic-grade stainless steel tubing packed with 60/80 mesh deactivated glass beads. The chromatographic column used for the C2-C12 hydrocarbon analysis was a 60 m long J&W DB-1 fused silica capillary column with a 0.32 mm inside diameter and 1 µm phase thickness. The oven temperature program was: -50 °C for 2 min, to 220 °C at 6 °C per min. Since the DB-1 column does not provide complete separation of the light C2 and C3 hydrocarbons, a separate analysis of the canister sample was performed to obtain accurate concentrations for ethane, ethylene, acetylene, propene, and propane. The chromatographic column used for this analysis was a J&W GS-Q fused silica capillary column with an internal diameter of 0.53 mm and a length of 30 m. The GC/FID response was calibrated in ppbC, using NIST Standard

Reference Material (SRM) 1805 (254 ppb of benzene in nitrogen). One ppm propane in a nitrogen standard (Scott Specialty Gases), periodically traced to SRM 1805, was used for calibrating the C2-C3 analytical system.

## RESULTS AND DISCUSSION

Figure 1 shows the traffic distributions in Bores #3 and #4 during the 11 one-hour runs (note that the number of vehicles on the y-axis is given in a logarithmic scale). It can be noted from these figures that the percentage of HDD traffic in Bore #4 is significant and it ranges from 3.4% for Runs 4 and 5 up to 68.5% for Run 2 and ~68% for Runs 8 and 10. The highest percentage of HDD traffic occurs early at the morning, between 0300 and 0500.

Figure 2 shows the comparison of the gas chromatographic traces for two Tenax samples, collected during Run 2 in Bores #3 and #4 (exit portals). Whereas the chromatograms for the Run 2 canister samples (C2-C12 hydrocarbons) collected in Bores #3 and #4 are not very different (traces not shown), the chromatograms of the Tenax samples show substantial differences in the intensity of C9-C19 hydrocarbons. The C9-C18 paraffins are much more abundant for the bore with 68.5% HDD traffic (Bore #4) than for the bore with only 1.8% HDD traffic (Bore #3).

Table I shows the TNMHC concentrations in the range of C2-C12, as quantified from canister samples, and corresponding TNMHC concentrations in the range of C2-C20, obtained from combining canister and Tenax data for Runs 4, 7, 8, and 9 (exit portal data only). In terms of traffic composition, these runs are representative of all 11 runs. The ratio of TNMHC in the C2-C20 range to TNMHC from the canister measurements represents the true TNMHC relative to the amount obtained from the canister alone. It is seen that if the SVHC are properly quantified (through Tenax measurements) the TNMHC estimates increase by 8 to 55% relative to what would be estimated from canisters alone.

**Table I. Assessment of the contribution of C10-C20 hydrocarbons to TNMHC in the range of C2-C20 from canister and Tenax measurements.**

Run #	Bore #	% Diesel <sup>a</sup>	Σ Canister HC C2-C12 ppbC	TNMHC <sup>b</sup> C2-C20 ppbC	TNMHC (C2-C20)
					Σ Canister HC
4	3	0.1	1606	1737	1.08
	4	3.4	2280	2501	1.10
7	3	1.0	863	963	1.12
	4	30.5	746	952	1.28
8	3	2.0	453	537	1.19
	4	68.0	325	505	1.55
9	3	1.0	1024	1172	1.14
	4	28.2	804	1135	1.41

<sup>a</sup> Diesel defined as heavy duty diesel trucks, diesel buses and light duty diesel autos.

<sup>b</sup> Data for exit portals only.

Table II shows the fleet average hydrocarbon emission rates (TNMHC, aliphatic and aromatic hydrocarbons) calculated for these four runs using canister data and combined Tenax plus canister data. Percent change represents the increase resulting from including SVHC in Tenax data. As can be seen from this table, SVHC account for a significant portion of diesel emissions; for Run 8 (Bore #4) with 68% diesel traffic, the addition of Tenax data increased the fleet average emission rate by 75%. Both aliphatic and aromatic hydrocarbon emission rates were increased significantly (70% and 82%, respectively). For runs dominated by light-duty spark

**Table II. Fleet Average Hydrocarbon Emission Rates [g/vehicle-mile] for Run 4, 7, 8, and 9.**

Run #	Bore #	% Diesel	TNMHC			Aliphatic*			Aromatic		
			C2-C12	C2-C20	% Change	C2-C12	C2-C20	% Change	C2-C12	C2-C20	% Change
4	3	0.1	0.91	0.99	8.7	0.59	0.60	1.7	0.32	0.39	21.9
	4	3.4	0.78	0.85	8.5	0.51	0.53	3.6	0.27	0.32	17.6
7	3	1.0	0.39	0.43	11.4	0.21	0.22	2.6	0.17	0.21	22.7
	4	30.5	0.75	0.97	29.5	0.43	0.51	18.1	0.32	0.46	44.9
8	3	2.0	1.29	1.52	17.8	0.68	0.74	8.6	0.61	0.78	28.2
	4	68.0	0.54	0.95	75	0.30	0.50	69.5	0.25	0.45	81.6
9	3	1.0	0.47	0.52	10.8	0.25	0.26	3.2	0.22	0.26	19.9
	4	28.2	0.74	1.04	40.7	0.48	0.58	19.4	0.25	0.46	81.7

\* Aliphatic include paraffinic and olefinic hydrocarbons.

ignition traffic, the addition of the SVHC portion of emissions does not significantly increase the emission rates (8% to 10% increase). However, the aromatic hydrocarbon emission rate from gasoline vehicles increased more, by ~20%, as the result of including Tenax data.

## CONCLUSION

Hydrocarbons in the range of C10-C20 (SVHC) are important components of the total hydrocarbons emitted from heavy duty diesel vehicles. They should be included in the calculation of diesel vehicle emission rates.

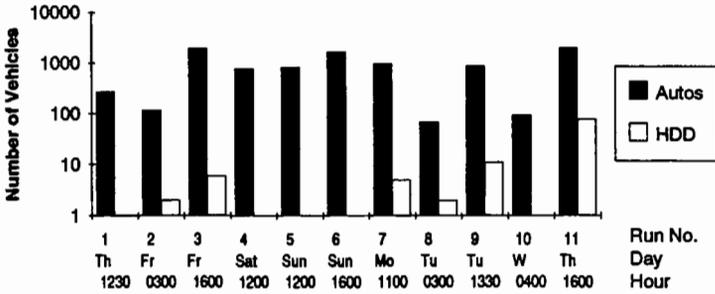
## ACKNOWLEDGEMENTS

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**Bore 3 Ft. McHenry Tunnel  
June 18-24, 1992**



**Bore 4 Ft. McHenry Tunnel  
June 18-24, 1992**

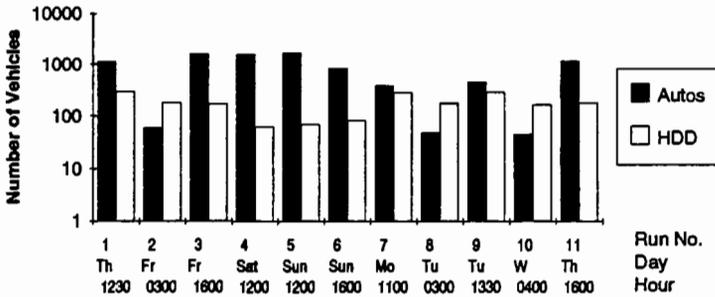
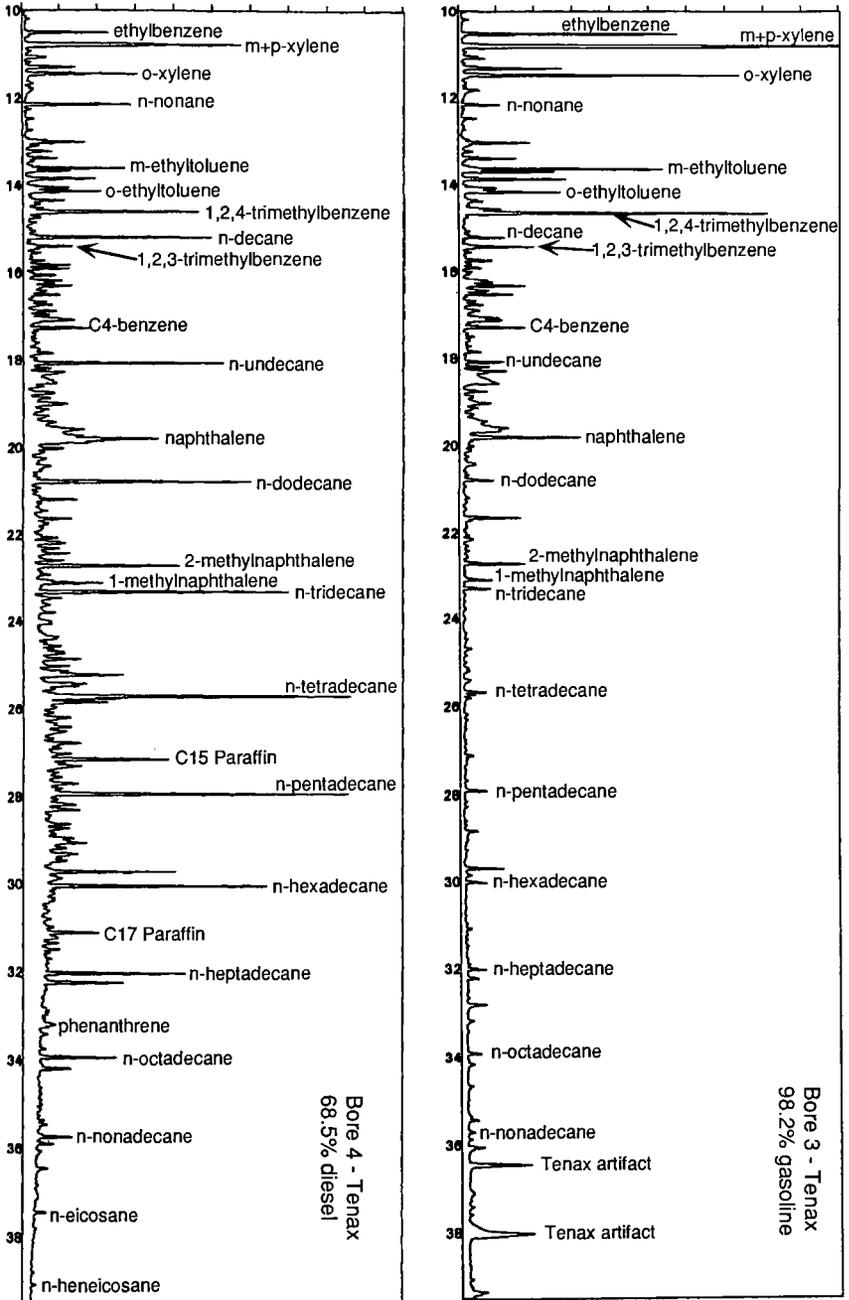


Figure 1. Traffic distribution in Bore #3 and Bore #4 during eleven one-hour runs (run number, day of the week, and sampling starting time are marked below the x-axis). Note that the ordinate scales are logarithmic.

Figure 2. Comparison of Bore 3 and Bore 4 Tenax chromatograms from Ft. McHenry Tunnel.



## MODELING THE ATMOSPHERIC FORMATION AND DECAY OF GAS AND PARTICLE BOUND NITRO POLYCYCLIC AROMATIC HYDROCARBONS

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### ABSTRACT

A method to study and model polycyclic aromatic hydrocarbons (PAH) and nitro-PAH (NPAH) formation and decay on the gas and particle phase in the atmosphere has been outlined. Diesel exhaust emissions were added and diluted into a 190 m<sup>3</sup> outdoor smog chamber and permitted to age under conditions of daylight and darkness. Ozone (O<sub>3</sub>), nitrogen oxides (NO<sub>x</sub>), volatile hydrocarbons in the gas phase were monitored. A sampling train consisting of annular denuder, filter and polyurethane (PUF) or XAD resin was used for the collection of gas and particle phase PAH and NPAH. Based upon the results, the current denuder design has sufficient flow (20 l/min) and adsorption characteristics for collection of PAH and NPAH in the chamber studies. Sampling artifacts were determined by comparison of the conventional sampling system and denuder system results. In general, the lower molecular weight PAH, such as naphthalene, acenaphthylene (ACE), fluorene (FLN) and phenanthrene (PHE) displayed some tendency for volatilization during the sampling process; and negligible artifacts were observed for higher molecular PAH, such as benzo(a)pyrene (BaP). Three or four-ring compounds, such as fluoranthene (FL) and pyrene (PY), exhibited both negative and positive artifacts which depended largely on the sampling conditions and temperature.

A reaction mechanism for PAH and NPAH has been further tested by comparison with chamber results. Simulations for FL and PY in gas phase were close to chamber observations, but sometimes we could not model the behavior of particle phase FL, PY or 1NPY. This may occur because PAH and NPAH inside of the particle and is not available for reaction with sunlight. No particle-associated compounds were found on the denuder, which implied that 2NFL or 2NPY was deposited on the particle immediately after formation in the photochemical processes in the gas phase. 2NPY and 2NFL simulations were generally good. Modeling results suggest that the addition of NO<sub>2</sub> to the gas phase adduct of FL + OH or PY + OH was the main reaction for NPAH formation. NPAH loss on particles could be simulated with a photo-induced reaction keyed to solar intensity.

### INTRODUCTION

NPAH have been observed in automobile emissions and other industrial processes<sup>1-4</sup>. It is recognized that in addition to being directly emitted, NPAH can be formed by the reactions of PAH with gaseous nitrogenous pollutants<sup>5-10</sup>. Over the past several years significant advances have been made in our understanding of the kinetics and reactions associated with the formation and degradation of NPAH in the atmosphere. Most studies have shown that the gas phase reaction of PAH with OH radicals is the primary processes for the formation of NPAH in the atmosphere<sup>6,7,9,10</sup>. To provide a better understanding of PAH and NPAH in the atmosphere, a mechanism was proposed in 1991<sup>10</sup> and further modified and evaluated in this study using outdoor chamber experiments with diesel exhaust (Table 1). Modeling results from this initial effort<sup>10</sup> demonstrated that it was possible to combine reactions of PAH and NPAH with a well established photochemical smog mechanism.

One of the short comings of our initial study was the inability to measure semi-volatile PAH and NPAH distributed between the gas and "particle" phase<sup>14-18</sup>. This was because a conventional sampling system with a filter and a back-up polyurethane foam (PUF) sorbent was used. Attempts to determine PAH gas/particle distribution by single channel denuders<sup>18</sup> and annular denuders<sup>19</sup> have been reported. Vapor phase components are removed by the denuder prior to the filter, and the particulate matter is collected on a filter. Any material "offgassing" from the particulate matter is trapped in an adsorbent which is placed downstream of the filter. More recently, Gundel et al.<sup>20</sup> have developed a denuder coating technique which permits the direct extraction and analysis of collected organics from the denuder. Based on this work<sup>20</sup>, we have modified the denuder by adding more channels and increasing the length to increase the adsorptive capacity. This paper describes: (1) the use of annular denuders to determine the phase distribution of PAH and NPAH in the smog chamber experiments; (2) sampling artifacts investigated by comparing the denuder sampling system and the traditional sampling system; and (3) chamber simulation results with a slightly modified PAH and NPAH mechanism.

### EXPERIMENTAL METHODS

Diesel exhaust from a 1967 Mercedes sedan (200D) engine was added and diluted into a 190 m<sup>3</sup> outdoor Teflon film smog chamber located in Pittsboro, NC, USA<sup>10</sup>. Concentrated diesel exhaust was added to the chamber for 30-60 seconds. The engine was in an idle mode during the chamber injection process. The particle concentration in the chamber was in the range of 200-600 µg/m<sup>3</sup>, and NO<sub>x</sub> generated from the combustion ranged from 0.4 to 0.7 ppm. To create active photochemical conditions, extra propylene gas was added into the chamber after the addition of diesel exhaust. Samples were collected by two 20 cm 4-channel annular denuders

in series or a 40 cm 5-channel denuder (ID=1.9 cm with 0.2 cm space), followed by a 47 mm Teflon impregnated glass fiber filter (type T60A20, Pallflex Products Corp., Putnam, CT) and a 8 x 2.5 cm PUF cartridge or a 4 x 0.9-cm-i.d. stainless steel tube cartridge filled with XAD-2 (Supelco, Inc., Bellefonte, PA; 16/50 mesh). The efficiency of the 20 cm denuder was greater than 89% for FL and PY at a sampling flow rate of 30 l/min. 85% of FL and PY were in the gas phase under these conditions. After taking the samples, the denuder was extracted four times with 30 ml of 2:1 hexane and acetone in field. The denuder then dried with pure nitrogen gas and was reused. PUF and filter samples were Soxhlet extracted in methylene chloride (MeCl<sub>2</sub>) for 8-12 hours and fractionated via normal phase high pressure liquid chromatography<sup>8,10</sup>. The samples subsequently were analyzed on a gas chromatography/mass spectrometer. The analytic methods are described elsewhere<sup>8,10</sup>.

## RESULTS AND DISCUSSION

### Sampling Artifacts

Two afternoon experiments were conducted in July and September, 1992 at our smog chamber facility in Pittsboro, NC<sup>10</sup>. The first experiment was performed on July 14, 1992. Two 20 cm denuders in series were used for gas phase PAH and NPAH collection. The sampling flow rate was 30 l/min. The most important observation was that no 2NFL, 1NPY or 2NPY was found on the denuder. This implied that 2NFL and 2NPY deposited on particles immediately after they formed in the gas phase. This observation strongly suggested that NPAH observed on PUF samples in previous experiments resulted from blow-off from the filters. In addition, no other typically particle associated compounds like benzo(a)pyrene (BaP) and Dibenz(a,h)anthracene (Di-BaA) were found on the denuder.

A parallel sampling system consisting of a 47 mm Teflon impregnated glass fiber filter and an 8 x 2.5 cm PUF cartridge was used for the first two samples in this experiment to determine the extent to which sampling artifacts occurred with the conventional sampling system. The particle concentrations for the denuder system and the filter/PUF system are compared in Figure 1(a). Extensive volatilization (negative artifact, 30-97%) was observed for more volatile compounds, such as acenaphthylene (ACE), fluorene (FLN) and phenanthrene (PHE) (saturated vapor pressure over a pure solid are  $6.7 \times 10^{-3}$  to  $6 \times 10^{-4}$  torr at 25°C); 15-37% negative artifact occurred for FL and PY (saturated vapor pressure over a pure solid is  $9.2 \times 10^{-6}$  and  $4.5 \times 10^{-6}$  torr, respectively), and negligible artifacts for higher molecular weight PAH, such as BaP (saturated vapor pressure over a pure solid is  $5.6 \times 10^{-9}$  torr).

Another experiment was carried out on September 13, 1992. A 40 cm 5-channel denuder was used for gaseous PAH and NPAH collection in place of the two 20 cm denuders. Again, in almost all the samples, no 2NFL, 1NPY or 2NPY was observed on the denuder. The exception was 2NFL, which was found on first denuder sample. Either gaseous 2NFL formed from some very rapid undetermined process or this sample was contaminated. No other typically particle-associated compounds were found on the denuder samples. In order to further evaluate the sampling artifacts, a parallel sampling system with a filter and an 0.9 x 4 cm XAD-2 trap was used. The filter concentrations in filter+XAD system and in denuder+filter+XAD system are shown in Figure 1(b). Negative artifacts were observed for ACE and FLN; and negligible artifacts for less volatile compounds. The most interesting finding was a 20-80% positive artifact rather than the negative artifacts observed for FL and PY shown in Figure 1(a). An 18-37% positive artifact was also observed for FL and PY in a winter experiment (February 10, 1992, temperature was 10°C). Sampling artifacts depend on temperature and sampling conditions<sup>17</sup>. The temperature in the September 1992 experiment (30°C) was lower than that (40°C) in the July 1992 experiment; thus, the effect of volatilization was lower in the September experiment. Additionally, the sampling flow rate was 15 l/min in both the February and September experiments. It was observed that when the filter face velocity decreased, the adsorption on the filter increased<sup>17</sup>. Pressure drops across the filter were found to be linearly proportional to the square of face velocity. As the pressure drop decreased, the adsorption effect should increase. The face velocity was 28.8 cm/s in the July experiment, and 14.4 cm/s in September and February experiment. Measurements of the pressure drop across the filter at the 15 l/min and 30 l/min showed values of 7.35 and 29.1 inches of water, respectively. For this sampling system it appears that for most volatile compounds, such as ACE and FLN, vapor pressures are so high that volatilization of collected compounds from filters overwhelms the adsorption effect (positive effect); for moderate volatile compounds, such as FL and PY, adsorption becomes significant and a positive sampling artifact appears.

### Simulation of Chamber Experiments

The first outdoor smog chamber experiment began at 2:30 pm on July 14, 1992. One minute of diesel soot was injected into 190 m<sup>3</sup> smog chamber at 2:37 pm, 0.4 ppmV propylene and 0.6 ppmV NO was added into the chamber after the addition of diesel soot, and a 260 µg/m<sup>3</sup> particle was generated in the chamber. The maximum concentration of O<sub>3</sub> was 0.26 ppmV, and the maximum modeled concentration of OH radical was  $1.65 \times 10^{-7}$  ppmV. The experimental data and simulation results for NO<sub>x</sub> and O<sub>3</sub> are shown in Figure 2(a).

A comparison between data and model prediction for gas and particle phase FL and PY is given in Figure 3. Simulation results for gas phase PY and FL agreed very well with observed results, but the model

overpredicted the loss rate of particle phase FL and PY. This may be attributed to a nonexchangeable fraction of FL and PY inside of the particles which is unavailable for reaction. Similar behavior for 1NPY was observed in the chamber. 1NPY emitted directly from diesel engine and like FL and PY, maybe distributed throughout the particles. In contrast to 1NPY, particle 2NPY reacted rapidly in the chamber and the simulation results fitted these data well (Figure 4). This is because most 2NPY was formed in the photochemical processes. After formation gaseous, 2NPY condensed onto particles and probably remained for the reaction period on or close to the exterior part of the particles (Figure 4).

To model our experimental data, a model yield for 2NFL of 0.076 from the reaction of FL + OH was used in the mechanism rather than 0.03 reported by Atkinson et al.<sup>11</sup> (Atkinson et al.<sup>11</sup>, however, reported a factor of 3 uncertainty in this yield). Using this higher yield permitted a lower photolysis rate for 2NFL than previously used<sup>10</sup> and this was more consistent with current peri-hydrogen theory of NPAH photostability<sup>21</sup>. Model results suggest that addition of NO<sub>2</sub> to the gas phase adduct of FL + OH or PY + OH is the main pathway for 2NFL and 2NPY formation, and the photolysis is the dominant loss process for NPAH.

Another experiment was carried out on September 13, 1992. Similar initial conditions to the July 14, 1992 experiment were used except higher NO<sub>x</sub> was added into the chamber. 0.52 ppmV propylene was added into the chamber at 12:42 pm. Then diesel exhaust was added into the chamber for 2.5 minutes at 1:30 pm, and 600 µg/m<sup>3</sup> of suspended particles appeared in the chamber. The total NO<sub>x</sub> concentration was 1.24 ppm. Simulation results of the NO<sub>x</sub> and O<sub>3</sub> behavior are shown in Figure 1 (b).

Gas and particle phase PAH simulations are given in Figure 5. Reasonable fits were obtained for gas phase FL and PY. For particle phase PY, and especially FL, the model predicted much faster decay than what was observed in the chamber. As in the previous experiment, we have surmised that a significant fraction of FL might not be available for reaction because it existed inside the particles. In order to confirm this point, we investigated the degradation of BaA and benzo(b)fluoranthene (BbF) which distribute mostly on the particle phase (Figure 6). BaA and BbF rapidly decayed at the beginning of the experiment and then appeared to be stable. This is similar to the behavior of particle FL and PY.

A yield of 0.1 for 2NFL was used in this experiment. Since this yield is at the upper most bound of the Atkinson proposed yield<sup>11</sup>, it is possible that some other processes for 2NFL formation is occurring.

#### ACKNOWLEDGMENTS

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TABLE 1. PAH AND NPAH REACTIONS

Gas Phase Reactions			k (min <sup>-1</sup> or ppm <sup>-1</sup> min <sup>-1</sup> )	Reference
1	PY <sub>(g)</sub> <sup>*</sup> + OH	PY-OH <sub>(g)</sub> + 0.005 x 2NPY <sub>(p)</sub>	72000	11
2	PY <sub>(g)</sub> -OH + O <sub>2</sub>		0.29	12
3	PY <sub>(g)</sub> + N <sub>2</sub> O <sub>5</sub>	1NPY <sub>(p)</sub>	0.81	11
4	FL <sub>(g)</sub> + OH	FL <sub>(g)</sub> -OH + 0.03 x 2NFL <sub>(p)</sub>	72000	11
5	FL <sub>(g)</sub> -OH + O <sub>2</sub>		0.29	12
6	FL <sub>(g)</sub> + N <sub>2</sub> O <sub>5</sub>	0.5 x 2NFL <sub>(p)</sub>	0.026	11
Particle Phase Reactions				
7	PY <sub>(p)</sub> + N <sub>2</sub> O <sub>5</sub>	1NPY <sub>(p)</sub>	0.01	8
8	FL <sub>(p)</sub> + N <sub>2</sub> O <sub>5</sub>	3NFL <sub>(p)</sub>	0.01	8
9	PY <sub>(p)</sub> {+hv}		0.045xk <sub>NO2</sub>	13
10	FL <sub>(p)</sub> {+hv}		0.02 x k <sub>NO2</sub>	13
11	PY <sub>(p)</sub> + O <sub>3</sub>		0.005	10
12	PY <sub>(p)</sub> + O <sub>3</sub>		0.005	10
13	1NPY <sub>(p)</sub> {+hv}		0.03 x k <sub>NO2</sub>	10
14	2NPY <sub>(p)</sub> {+hv}		0.045xk <sub>NO2</sub>	
15	2NFL <sub>(p)</sub> {+hv}		0.02xk <sub>NO2</sub>	

\*All gas phase PAH were lost to the walls at a rate of 0.0021 min<sup>-1</sup>, particle PAH and NPAH were removed at a rate of 0.0013 min<sup>-1</sup>.

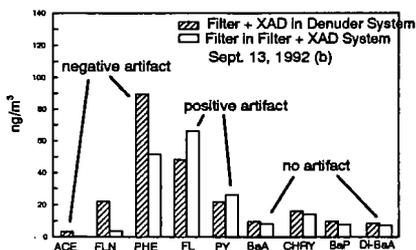
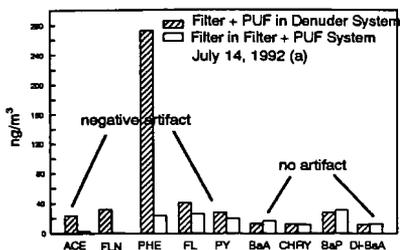


Figure 1. Comparison of Particle Concentrations of PAH in Two Sampling Systems

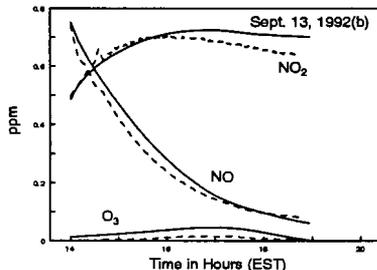
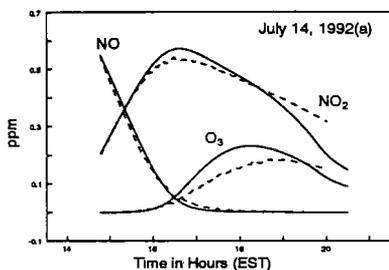


Figure 2. O<sub>3</sub>, NO and NO<sub>2</sub> Model Simulation Results and Data. Dash lines are data and solid lines are model simulations (same for the other graphs).

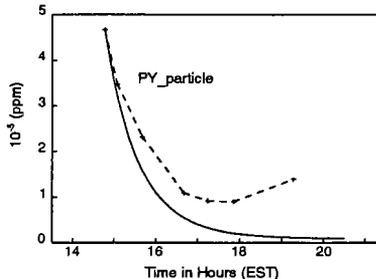
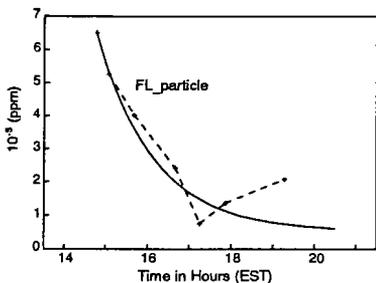
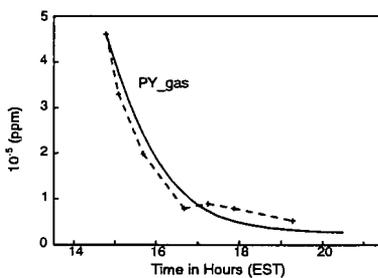
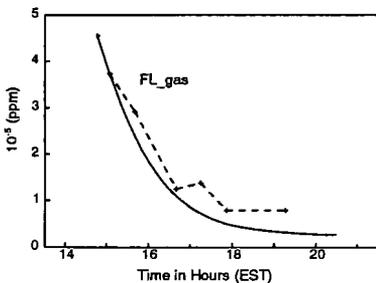


Figure 3. Data and Simulation Results for Gas and Particle Phase FL and PY (July 14, 1992)

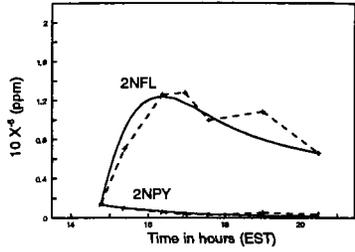
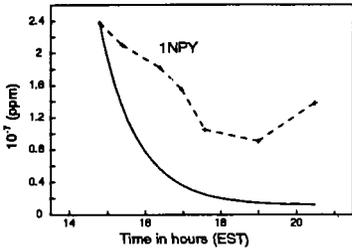


Figure 4. Model Simulations and Data of 1NPY, 2NPY and 2NFL in Particle Phase (July 14, 1992)

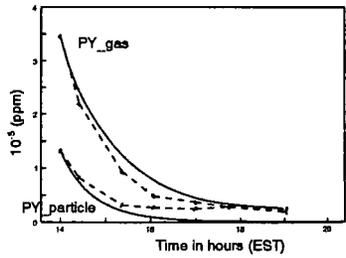
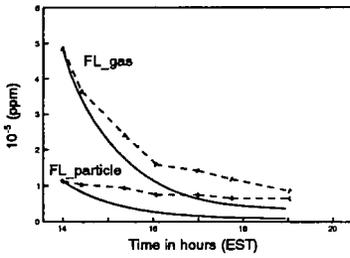


Figure 5. Data and Simulation Results for Gas and Particle Phase FL and PY (Sept. 13, 1992)

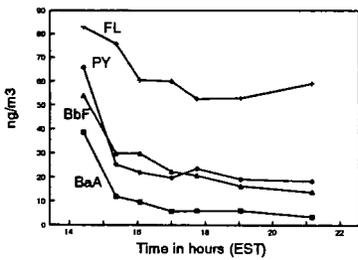


Figure 6. Behavior of FL, PY, BaA and BbF in Particle Phase (Sept. 13, 1992)

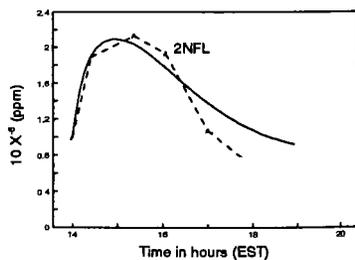


Figure 7. Data and Model Simulations for 2NFL (Sept. 13, 1992)

## EFFECT OF COMBUSTION TEMPERATURE ON THE ATMOSPHERIC STABILITY OF POLYBROMINATED DIBENZO-*p*-DIOXINS AND DIBENZOFURANS

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### ABSTRACT

The incineration of materials containing polybrominated diphenyl ether (PBDPE) flame retardants can potentially lead to the formation of polybrominated dibenzo-*p*-dioxins and dibenzofurans (PBDDs and PBDFs). Some of these compounds may exhibit toxicities similar to those of their chlorinated analogues. Little is known about the atmospheric stability of PBDDs and PBDFs. In this study PBDDs and PBDFs produced from the combustion of polyurethane foam (PUF) containing 4.4% PBDPEs were injected into outdoor Teflon film chambers and aged in the presence of sunlight under typical atmospheric conditions. Incineration experiments with combustion temperatures in the range of 400-450°C were categorized as "low temperature" experiments and those in the range of 670-780°C as "high temperature" experiments. PBDDs and PBDFs have been found to occur predominantly in the particulate phase, thus filter samples were collected over time to ascertain the atmospheric stability of these compounds. Production of PBDFs, namely, tetrabrominated dibenzofuran (TBDF) and pentabrominated dibenzofuran (PeBDF) and decay of tetrabrominated-*p*-dioxin (TBDD) was observed in "low temperature" experiments. Production of TBDF and PeBDF is believed to occur from photolysis of unburned PBDPEs. TBDF, PeBDF and TBDD emissions from "high temperature" experiments were stable. Validation of PBDF and PBDD behavior was done by collecting particulate- and gas-phase samples of polycyclic aromatic hydrocarbons (PAHs). Particle-bound PAHs from "low temperature" experiments degraded while corresponding PAHs from "high temperature" experiments were stable. Particle formation and composition from the two kinds of experiments have been investigated to explain these differences. These observations suggest that under typical incinerator conditions particulate-bound emissions of these compounds will be transported over long distances due to long half-lives. Incineration temperatures around 450°C can lead to unstable emissions with atmospheric half-lives of 1-2 h. The dependence of the atmospheric stability of incineration-generated pollutants on the combustion temperature is an important finding of this study.

### INTRODUCTION

Incineration has been projected as an attractive waste disposal technology. This projection is underscored by the fact that since 1979, 3500 landfills have been closed and within the next five years landfill capacity will exist for only 20 million tons for the anticipated 160 million tons of waste generated.<sup>1</sup> Concomitant to the likely increased use of incineration is the growing production of brominated organics, particularly with respect to PBDPEs which is used as fire retardants in textiles, plastics, carpets and other materials.<sup>2</sup> Incomplete combustion of these brominated organics present in municipal waste can lead to the formation of PBDDs and PBDFs. Therefore, it is expected that atmospheric concentrations of PBDDs and PBDFs will rise in the future in light of the increasing production of brominated compounds. While much attention has been given to polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDDs and PCDFs), animal studies have shown that PBDDs and PBDFs are at least as toxic as their chlorinated analogues.<sup>2</sup>

Central to biological exposure and uptake of PBDDs and PBDFs is their atmospheric fate and transport. Atmospheric lifetime, itself can vary depending on the nature of combustion-generated emissions, which is dependent on combustion variables like combustion temperature, residence time, oxygen concentration and other parameters. Operating combustion temperatures in incinerators have been found to vary from 300-1300°C, although typical operating temperatures are around 800°C.<sup>3</sup>

An important consideration in determination of the atmospheric stability of semi-volatile organics like PBDDs and PBDFs is their gas-particle partitioning. Theoretical predictions using an equation developed by Junge<sup>4</sup> and experimental observations by Lutes et al.<sup>5</sup> revealed that more than 95% of PBDDs and PBDFs occur on particulate-phase. Thus, the atmospheric stability of PBDDs and PBDFs is primarily relevant to their occurrence on atmospheric aerosols as opposed to their presence in gas-phase.

Currently, there exists a paucity of data on photodegradation of PBDDs and PBDFs under realistic conditions. Laboratory studies have been carried out in organic solutions or on solid substrates. An important observation regarding these experiments is the rapid decay of 2,3,7,8-TBDD and 2,3,7,8-TBDF in *i*-octane (half-lives 0.8 min and 0.7 min respectively) and relative stability on quartz surface (half-lives 32 h and 35 h respectively).<sup>6</sup> Given such numbers it becomes all the more imperative to arrive at representative values for atmospheric half-lives of PBDDs and PBDFs using outdoor chambers. Preliminary work in this direction revealed that incineration of PUF containing PBDPEs at combustion temperatures ranging from 640-760°C yielded particulate-bound PBDDs and PBDFs which were relatively stable.<sup>5</sup> This implies that combustion under these conditions yields PBDDs and PBDFs that photodegraded at rates comparable to solid-phase laboratory experiments. In this study incineration experiments were carried out with PUF containing PBDPEs

at combustion temperatures ranging from 400-780°C and atmospheric stability of PBDDs and PBDFs were determined. PAHs generated from these experiments were also quantified to gain a better insight into the behavior of PBDDs and PBDFs. Results from a "low temperature" and a "high temperature" experiment have been included in this article. Results were verified by performance of another set of experiments.

## EXPERIMENTAL SECTION

Incineration experiments were carried out in an ignition vessel shown in Figure 1. The combustion material consisted of PUF containing 4.4% w/w of industrial grade DE-71 mixture (40% TBDPE, 57% PeBDPE and 3% HxBDPE). Experiments carried out with combustion temperatures ranging from 400-500°C were categorized as "low temperature" experiments and those in the range of 650-800°C as "high temperature" experiments. Emissions from the prototype incinerator were directed into outdoor smog chambers located in Pittsboro, NC and have been described elsewhere.<sup>7</sup> The emissions were allowed to age within the chamber atmosphere for approximately 4 h. During this time, particulate samples were collected by passing chamber air through a sampling train containing a 47-mm T60 A20 Teflon-impregnated glass fiber filter, followed by a 4 in. X 1.5 in. PUF cartridge for collection of vapor-phase species. Chamber ozone, nitrogen oxide, relative humidity and temperature were monitored during the course of an experiment. Total solar radiation was measured by using a black and white pyranometer and dilution rate was measured by an SF<sub>6</sub> tracer. Electrical Aerosol Analyzer (EAA, TSI Inc., MN) and Laser Aerosol Spectrometer (LAS, PMS Inc., CO) were used to gather data on size distribution of the combustion-generated particles. In addition, nucleopore filter samples were also collected, which were later analyzed with a Scanning Electron Microscope (SEM) and the resulting photographs were used to describe particle morphology.

Particulate samples were analyzed for PBDDs and PBDFs in accordance with EPA method 8290.<sup>8</sup> Briefly, this involved extraction of the samples in toluene and enrichment using three sets of columns: silica gel, florisil and carbon/celite. All laboratory work was carried out under artificial lights, shielded against UV radiation, and samples were kept wrapped in foil to preclude photodegradation of the analytes in the laboratory. Quantification of PBDDs and PBDFs was achieved by internal standardization using <sup>13</sup>C<sub>12</sub> labeled compounds. The samples were analyzed by high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS). The analysis was carried out in the Selected Ion Monitoring (SIM) mode at a resolution of 10,000. Procedure for PBDE analysis was similar to the one for PBDD and PBDF analysis, except that carbon column was excluded in the chromatographic cleanup process<sup>9</sup>. Samples for PAH analysis were extracted in dichloromethane and analyzed by HRGC/HRMS in the SIM mode at a resolution of 10,000. β,β-binaphthyl was used as the internal standard for quantifying PAHs.

## RESULTS AND DISCUSSION

### PBDD, PBDF & PAH Analysis:

The compounds detected were TBDD, TBDF and PeBDF. Detection of individual isomers was not possible due to lack of appropriate standards. Hence, results have been presented in terms of the total concentration of a compound and not in terms of specific isomers. Two "high temperature" experiments were carried out to demonstrate that earlier results could be repeated. For these experiments, plots of chamber concentrations of TBDD, TBDF and PeBDF versus chamber aging time had insignificant slopes at a 90% level of confidence. Figures 2a, 2b and 2c include the plots of these compounds from one of the experiments with a similar trend for the other experiment. Therefore, it can be concluded that there is no evidence of decay for PBDF and PBDD emissions from "high temperature" incineration experiments. These results are similar to those obtained by Lutes et al.<sup>5</sup> However, in "low temperature" experiments, there is decay in TBDD concentration yielding half-lives of 1-2 h. Figure 3a is a plot of TBDD concentration versus time for one of the "low temperature" experiments. Photodegradation rates in solid-phase and solution-phase laboratory experiments is somewhat analogous to our "high temperature" and "low temperature" experiments. Figures 3b and 3c include plots of chamber concentrations of TBDF and PeBDF versus chamber aging time from one of the "low temperature" experiments. Significant positive slopes imply the production of these compounds over time in the chamber atmosphere. PAHs exhibited a trend similar to TBDD for "high temperature" and "low temperature" experiments (Figures 4, 5, 6 & 7). In the latter case, PAHs like phenanthrene, fluoranthene and pyrene had half-lives of 1-2 h. Experimental conditions for the experiments mentioned in this article are presented in Table 1.

The lack of agreement in TBDD and PAH behavior for the two kinds of experiments may be attributable to differences in physical and chemical properties of the combustion-generated particles. It was observed that the color of particles in "high temperature" experiments was dark brown or black in stark contrast to the light brown color in "low temperature" experiments. Investigators have mentioned that darker substrates can absorb most of the incident light and reflect little to cause photodegradation of the compounds adsorbed on it.<sup>10</sup> Also, particles from "low temperature" experiments may have a higher specific surface area (SSA) to absorb more light, thereby yielding higher rates of photolysis.<sup>11</sup> Drawing an analogy from the laboratory experiments suggests that the presence of an organic layer in "low temperature" particles may expedite photodegradation, similar to the solution-phase experiments. An illustration of this concept is provided in Figure 8. The organic layer may be formed from the PUF vapor that was left uncombusted.

Contrary to degradation of TBDD in "low temperature" experiments, production of TBDF and PeBDF was observed for these experiments. We believe that this was the result of photolysis of unburned PBDEs which photolyzed

to yield TBDF and PeBDF. Buser<sup>12</sup> found that thermolysis of PBDPEs at 510°C caused 10% destruction of the ethers as opposed to 96-97% destruction at 650°C. Therefore, it is expected that almost 90% of the PBDPEs will be left uncombusted in our "low temperature" experiments. Choudhry et al.<sup>13</sup> have reported 14% yield of tetrachloro dibenzofuran (TCDF) over a 4 h period from photolysis of pentachloro diphenyl ether (PeCDPE) dissolved in cyclohexane. Extrapolating this to our system facilitated mass balance calculations and revealed that there is degradation of TBDF (half-life 4h) if the confounding factor due to its production from photolysis of unburned ethers was taken into account.

#### **Comparison of Particle Characteristics:**

Analysis of particle distribution data evinced that there was not a significant difference in SSA for the particles generated from the two kinds of experiments, thus eliminating higher SSA as a plausible explanation for rapid photodegradation in case of "low temperature" experiments. Examination of SEM photographs indicated that particle morphology differs largely for the "low temperature" and "high temperature" experiments. The former is characterized by singular and spherical particles, while the latter distinguishes itself by the presence of coagulated masses. This information was used to prescribe a model for particle formation by taking into account the different combustion temperatures (Figure 9).<sup>14</sup> According to this model, particle formation in "low temperature" conditions is dominated by nucleation and condensation. The presence of agglomerates in "high temperature" conditions is the result of formation of reaction products that coalesced with fly ash or other reaction products to form agglomerates. Such a model for particle formation in incinerators would also espouse our supposition regarding the presence of an organic layer around "low temperature" particles.

To further enhance our understanding of particle composition, analysis was carried out to determine fraction of particulate mass that is extractable or particulate organic matter (POM). A larger POM should be associated with the particles generated from "low temperature" experiments as combustion process will not be very efficient leading to a larger concentration of products of incomplete combustion. POM can be correlated to the presence of an organic layer around the particles. This draws an analogy from comparison of wood soot (POM 80-90%) and diesel soot particles (POM 30-40%), wherein the former has a higher extractable mass and probably, an organic layer around it as wood soot particles lose their integrity when impacted upon a tin foil.<sup>15</sup> Percent extractable analysis showed that for "low temperature" particles the extractable mass was around 46% compared to 30% from "high temperature" particles. A higher fraction of extractable mass in the "low temperature" particles can be linked to the presence of unburned PUF that manifested itself in the form of an organic layer around the particles.

#### **CONCLUSIONS**

Typical operating conditions in incinerators may lead to air emissions which can be transported over long distances due to the stable nature of the emissions. This study demonstrates that lower combustion temperatures can lead to the formation of toxic air pollutants like PBDDs, PBDFs and PAHs that may be relatively unstable in the environment. The dependence of half-lives of incineration-generated air pollutants on the combustion temperature should be taken into account for accurate prediction of biological exposure. Experiments should be carried out with a heterogeneous system as is the case in municipal waste combustors, where the dynamics of particle formation can be more complex. Characterization of the products of photodegradation will aid in determination of the toxicity of the products and in postulation of the mechanism of photolysis. It should be stated that while lower combustion temperatures can be beneficial due to shorter half-lives of toxic air pollutants but they will not lead to significant reduction in waste volume, one of the primary objectives of incineration.

#### **ACKNOWLEDGMENTS**

We want to thank Tom Merz for his help in conducting combustion experiments, G. Dean Marbury for assistance in mass spectrometry analyses and Dr. Bob Bagnell for assistance in scanning electron microscopy. Funding for this project was received from The Office of Exploratory Research, Washington, D.C. (Grant# R-817534).

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TABLE 1. COMPARISON OF EXPERIMENTAL CONDITIONS

	"LOW" TEMP.	"HIGH" TEMP.
COMBUSTION TEMP. (°C)	470	780
CHAMBER TEMP. (°C)	23.9-27.4	19.5-22.2
RELATIVE HUMIDITY (%)	42-39	10-13
AVG. TOT. SOLAR RADIATION (cal./cm <sup>2</sup> /min.)	0.86	0.63
[NO] (ppm)	0-0.016	0-0.074
[NO <sub>2</sub> ] (ppm)	0.01-0.026	0.01-0.061
[O <sub>3</sub> ] (ppm)	0-0.041	0-0.06
INJECTION TIME	10:15 a.m.	11:00 a.m.

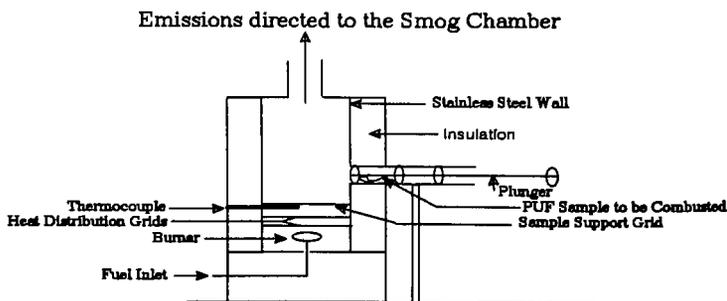


Figure 1. SECTION OF THE IGNITION VESSEL

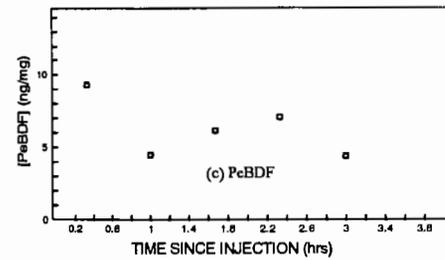
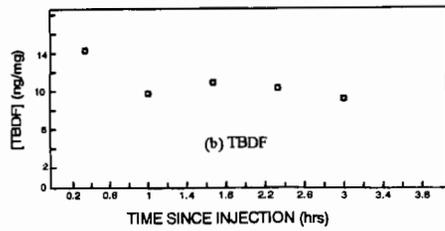
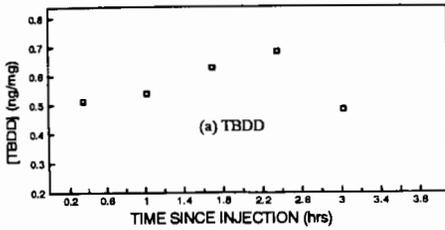


Figure 2. CHAMBER CONCENTRATIONS OF TBDD, TBDF & PeBDF FOR "HIGH TEMPERATURE" EXPERIMENT

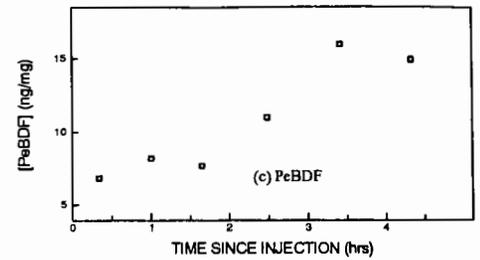
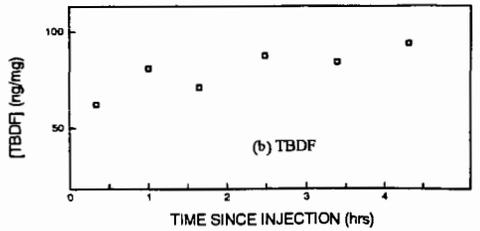
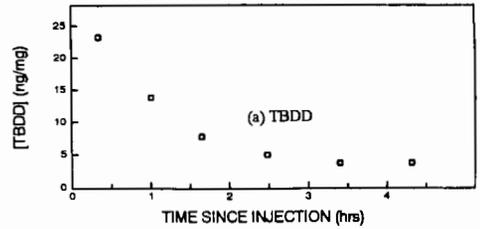


Figure 3. CHAMBER CONCENTRATIONS OF TBDD, TBDF & PeBDF FOR "LOW TEMPERATURE" EXPERIMENT

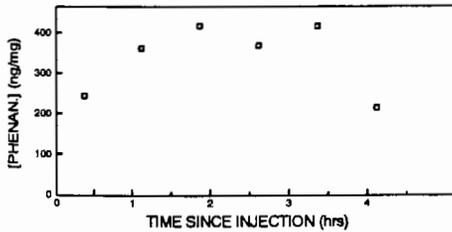


Figure 4. CHAMBER CONCENTRATION OF PHENANTHRENE VERSUS AGING TIME FOR "HIGH TEMPERATURE" EXPERIMENT

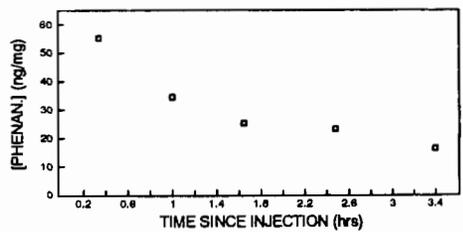


Figure 5. CHAMBER CONCENTRATION OF PHENANTHRENE VERSUS AGING TIME FOR "LOW TEMPERATURE" EXPERIMENT

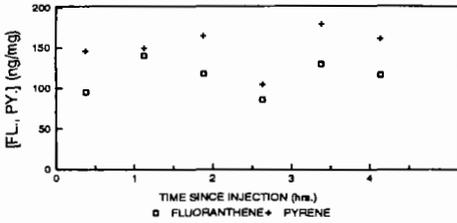


Figure 6. CHAMBER CONCENTRATIONS OF FLUORANTHENE AND PYRENE VERSUS AGING TIME FOR "HIGH TEMPERATURE" EXPERIMENT

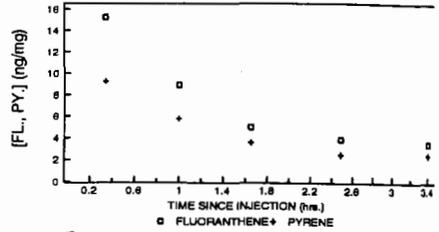
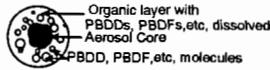


Figure 7. CHAMBER CONCENTRATIONS OF FLUORANTHENE AND PYRENE VERSUS AGING TIME FOR "LOW TEMPERATURE" EXPERIMENT

"LOW TEMPERATURE" PARTICLE



"HIGH TEMPERATURE" PARTICLE

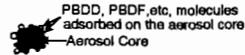


Figure 8. POSTULATED COMPOSITION OF PARTICLES GENERATED FROM COMBUSTION EXPERIMENTS

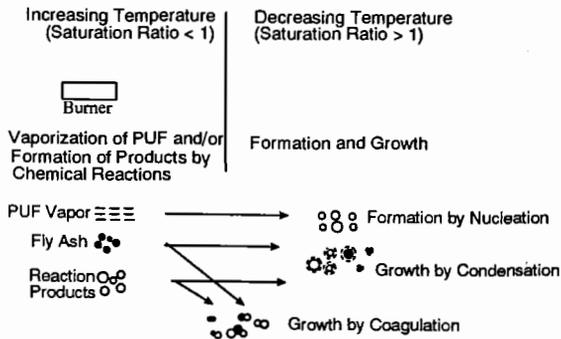


Figure 9. SCHEMATIC OF THE BURNER SHOWING PARTICLE FORMATION AND GROWTH MECHANISMS

## A METHOD FOR STUDYING HETEROGENEOUS PHOTOCHEMICAL REACTIONS OF POLYCYCLIC AROMATIC HYDROCARBONS ON ATMOSPHERIC COMBUSTION AEROSOLS

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### ABSTRACT

A photochemical turntable reactor was used to study photodegradation of polycyclic aromatic hydrocarbons in organic coatings on carbonaceous particle surfaces. This required the development of a technique to coat the particles with an organic layer and to evenly disperse the particles on a filter substrate. The technique has potential for use in determining differences in reaction rate constants, reaction products and reaction mechanisms. Previous researchers have noted that polycyclic aromatic hydrocarbon photodegradation can be strongly influenced by particle surfaces. Preliminary results suggest that benz(a)anthracene and benzo(a)pyrene photodegradation can also be influenced by other organic constituents associated with the particle coating.

### INTRODUCTION

Polycyclic aromatic hydrocarbons (PAH) on wood smoke react rapidly in sunlight, but are stable at night<sup>1</sup>. Photodegradation mechanisms of PAH associated with combustion particles are poorly understood. Although surface characteristics appear to strongly influence photodegradation of adsorbed PAH on silica and fly ash<sup>2</sup>, little is known about the effects of solid elemental carbon surfaces associated with more common U.S. PAH sources such as diesel soot or wood smoke. Moreover, recent experiments indicate that organic compounds associated with wood smoke also strongly influence PAH photodegradation rates. It follows that co-adsorbed reactive organic compounds or a particle organic layer should also be considered in experiments designed to measure photodegradation in organic coatings on particle surfaces. This work describes the development of an experimental technique to compare relative rates of PAH photodegradation in organic coatings on particle surfaces.

### APPROACH

A conventional photochemical turntable reactor for comparing relative photochemical reaction rates in solutions was adapted for studying reactions on atmospheric particles. This was accomplished by distributing the particulate matrix on filter surfaces and analyzing changes in concentration after irradiation at certain time intervals. Filters were mounted on specially constructed test-tube shaped filter holders which were placed in the turntable slots normally used to hold test tubes. This approach required a separate filter for each sample. For example, if samples were analyzed at one hour intervals for four hours, comparison of two particle coatings required preparation of eight filters for irradiation. A significant effort was therefore required to develop a technique to produce even organic coatings on the model particle surfaces and even dispersal of particles on the filters.

A model system was selected to test this approach. Carbon black particles were coated with an organic mixture consisting of isoeugenol (2 methoxy - 4 propenyl phenol), fluoranthene, benz(a)anthracene, benzo(k)fluoranthene, and benzo(a)pyrene. The system is simpler than real wood smoke or diesel soot to simplify measurement of photodegradation rates, analysis of products, and tests for reaction mechanisms. However, it retains the basic characteristics of many PAH containing combustion sources because it contains a solid, carbonaceous surface and a reactive organic compound which influences PAH photodegradation rates. Isoeugenol was chosen as the reactive organic species because of its abundance in wood smoke<sup>3</sup> and its known influence on PAH photodegradation<sup>4</sup>.

## EXPERIMENTAL

Figure 1 illustrates the methodology and apparatus used in this study. Carbon black particles coated with PAH or an isoeugenol/PAH solution mixture were dispersed on Gelman\* Zefluor\* Teflon membrane filters (Fisher Scientific) using vacuum filtration. Five irradiation experiments were carried out to investigate the influence of isoeugenol on PAH photodegradation in the presence of a carbonaceous surface. These are summarized in Table 1, which describes experiment duration, sampling interval, multicomponent mixtures used, and concentrations of the components in the mixture.

The organic mixture consisting of PAH and isoeugenol was dissolved in dichloromethane and sonicated for 1 minute. The dichloromethane solvent was evaporated, leaving a coating on the particles. The coated particles were suspended in 25 ml dichloromethane above a 47 mm Zefluor Teflon membrane filter in a Buchner funnel. The suspension was vacuum filtered, leaving the coated particles evenly distributed on the filters.

The particle loaded filters were then mounted on an ACE Glassware Photochemical Turntable Reactor equipped with a water cooled 450W high pressure Hg lamp. After irradiation the filters were extracted with dichloromethane in microsoxhlet extractors for 12 hours. Extracts were concentrated to 1 ml using a Kuderna-Danish apparatus, transferred to a tared vial, and evaporated to almost dryness under a stream of nitrogen. 100 to 400ul of acetonitrile were added and the samples were analyzed by reverse phase HPLC and GCMS.

In three of the experiments outlined in Table 1, photodegradation rates of PAH on carbon black were compared in the presence and absence of isoeugenol. In the fourth and fifth experiments photodegradation rates were compared between PAH dissolved in isoeugenol and guaiacol (2 methoxy phenol) coated on carbon black.

In the first experiment the lamp was placed in a borosilicate immersion well which filtered out radiation below 300nm. In the second and third experiments the 366 nm line of the Hg spectrum was isolated using optical filters and a quartz immersion well. The fourth and fifth experiments were performed using the borosilicate well. Similar experiments were carried out in the dark to verify that PAH decay was due to photodegradation and not volatilization or other chemical reactions.

Preliminary experiments indicated that PAH photodegradation proceeded more rapidly for PAH coated on bare Zefluor filters than on carbon black. It was consequently important to verify PAH and isoeugenol were not simply coated on the filter, but were in contact with the carbon black. To address this, recovery experiments were designed in which coated carbon black particles were deposited on a number of filters using the coating technique described above, which were designated as reference samples. On a second "filter only" set of an equal number of filters the same PAH solution was coated directly on to the filter by vacuum filtration. The fraction of PAH adsorbed on the filter, instead of the carbon black, is estimated from a "recovery ratio" defined as the ratio of the fraction of original PAH recovered from the "filter only" samples to that recovered from the reference samples. Coated samples were also inspected by scanning electron microscopy (SEM).

## RESULTS AND DISCUSSION

During the course of the research it became apparent that the concentrations of PAH and isoeugenol had a strong influence on whether the PAH solution was in contact with the carbon black or adsorbed on the filter. The filter/carbon black recovery ratios increased with increasing PAH/carbon black mass ratios, suggesting that as the capacity of the carbon black to sorb the PAH is approached, significant filter adsorption occurs. This was supported by SEM photographs, which showed that when isoeugenol mass was 30% of the carbon black mass, significant amounts of isoeugenol solution was coated on the filter rather than the carbon black. It was difficult to determine how much isoeugenol was coated on the filter at lower concentrations, but 30% appeared to be an upper limit for the isoeugenol to remain in contact with the particle surface. On the basis of the recovery and SEM experiments, isoeugenol amounts were maintained below 10% of the carbon black mass. The PAH concentration in

the stock solution was less than 1000 ng/ul. 400ul of stock solution was applied to 1mg of carbon black. The carbon black retains 2-5% of the PAH following vacuum filtration, resulting in an adsorbed PAH concentration of less than 20 ng/mg.

The results to the irradiation experiments give a preliminary indication that isoeugenol affects PAH photodegradation rate even in the presence of a carbonaceous surface. In the first experiment, decay was faster than for the next two experiments because more light was transmitted to the samples through the borosilicate well than when the optical filters were used. Decay appeared to be initially very rapid but ceased well before the end of the experiment. The initial rapid decay probably occurred because of the high light intensity. It is possible that photodegradation stopped early in the experiment because extractable PAH were hidden from exposure to light in the interstices of the carbon black. Benz(a)anthracene appeared to react more rapidly in the presence of isoeugenol. Benzo(a)pyrene was not recovered from carbon black particles which did not contain isoeugenol. In subsequent experiments a longer soxhlet extraction time of 12 hours enhanced the recovery of BaP from bare carbon black.

In the second and third experiments the observed reaction rates were slower because the optical filters only transmitted the 366nm wavelength which resulted in a decreased light intensity. The photodegradation in these experiments is described in figures 2 and 3. The rate constants were tested for parallelism<sup>5</sup> by comparing the first order rate expression for PAH photoreactivity on carbon black with isoeugenol present to the first order rate expression in the absence of isoeugenol for the same experiment. Rejection of the hypothesis of parallelism indicates the difference in the rate constant is statistically significant. In the second experiment the difference was not statistically significant for benz(a)anthracene ( $p > .1$ ) but was borderline for benzo(a)pyrene ( $.05 < p < .1$ ). For the third experiment statistical significance ( $p < .05$ ) was observed for both benz(a)anthracene and benzo(a)pyrene. One possible explanation for this apparent contradiction is that during the first three hours of irradiation the difference in concentrations is not significantly greater than experimental error, so a longer experiment duration is required to observe a significant difference in rate constants. No appreciable decay was observed in the presence or absence of isoeugenol when similar experiments were carried out in the dark.

The previously described experiments compared photoreactivity of relatively small amounts of PAH adsorbed on carbon black to PAH dissolved in a relatively large amount of organic liquid coated on to the carbon black. In the fourth and fifth experiments photodegradation in the carbon black coated isoeugenol solutions was compared to carbon black coated guaiacol solutions. This provided a comparison in which both systems contained PAH dissolved in an organic liquid coating. Guaiacol is structurally similar to isoeugenol, but solution experiments have shown that PAH react much more slowly in the presence of guaiacol than in the presence of isoeugenol<sup>4</sup>. Benz(a)anthracene reacted more rapidly in isoeugenol than in guaiacol on carbon black and benzo(a)pyrene reactivity also seemed slightly greater in isoeugenol. These observations also suggested that isoeugenol influences PAH photoreactivity in the presence of a carbonaceous surface. However PAH decay in the isoeugenol solutions appears to be slower than in previous experiments. This might be due to differences in concentrations between the experiments (see table 1). Experiments which had higher levels of isoeugenol recovered from the particles seemed to exhibit faster rates of PAH photodegradation.

The results of all five experiments suggested that compounds such as isoeugenol which accelerates PAH photodegradation in solution, might still accelerate PAH photodegradation even in the presence of carbonaceous surfaces. However, improvements in this technique are required before this can be considered conclusive. In most experiments statistical outliers reduced the precision in rate constant calculations. Variability in the measured PAH concentrations between samples was observed during the coating, exposure, and the extraction procedures. The average coefficient of variation was 16. This imprecision might be partially responsible for the apparent contradiction in the experimental data, which shows statistical significance for some experiments but not for others. Less problematic explanations are differences in irradiation time and concentration between experiments. However, more experimental effort is required before these explanations can be accepted. Finally, in spite of the

preliminary experiments reported here concerning filter adsorption, more effort is still needed to verify that significant photodegradation is not occurring in PAH adsorbed to the filter substrate itself.

## CONCLUSIONS

A technique was developed to compare relative photodegradation rates of PAH adsorbed to particulate matter on filters mounted on a photochemical turntable reactor. The technique can be used to investigate systems which are simpler than actual combustion particles, but which retain the characteristics of a solid carbonaceous surface coated with an organic layer. This potentially simplifies determination of rate constants, reaction products and reaction mechanisms. The technique was tested by comparing photodegradation of PAH in solutions of isoeugenol coated on carbon black to PAH coated on carbon black without isoeugenol. Preliminary results suggested that benz(a)anthracene and benzo(a)pyrene photodegradation was more rapid in isoeugenol solutions even in the presence of a carbonaceous surface. This is consistent with previously reported results of rapid PAH photodegradation in toluene solutions of isoeugenol and PAH. This suggests that although particle surface characteristics can strongly affect PAH photodegradation, organic constituents coated on particle surface are also important. Several improvements were identified which would further development of the technique to produce more conclusive results.

## ACKNOWLEDGMENTS

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Table 1. Summary of 5 Experiments

Compound	Initial Coating Concentration (ug/mg)		Photodegradation Rate Constants (hour <sup>-1</sup> )		Ratio of Rates	Significance of Rate Change p<.05
	w/ no iso	w/ iso	w/ no iso	w/ iso		
First Experiment, 8/11/92, Borosilicate Well, 1.5hr duration, .5 hr intervals						
Isoeugenol	0	.45		.17		
Fl	.43	.37	.28	.69	2.5	yes
BaA	.18	.15	.20	.27	1.4	yes
BkF	.36	.18	.04	.10	2.5	yes
BaP	none detected	.25		.18		
Second Experiment, 8/28/92, Quartz Well w/ light filter, 3hr duration, .75 hr intervals						
Isoeugenol	0	13.5		.89		
Fl	4.5	4.1	.24	.13	0.5	no
BaA	1.8	1.4	.08	.08	1.0	no
BkF	2.0	1.8	.02	.14	7.0	yes
BaP	3.0	2.9	.02	.13	6.5	yes
Third Experiment, 9/10/92 Quartz Well w/ light filter, 6hr duration, 1.5 hr intervals						
Isoeugenol	0	277		.23		
Fl	4.8	5.9	.11	.15	1.4	no
BaA	1.8	1.7	.05	.09	1.8	yes
BkF	2.3	2.1	.01	.04	4.0	yes
BaP	2.8	2.8	.01	.04	4.0	yes
Fourth Experiment, 2/05/93, Borosilicate Well, 3hr duration, .33 hr intervals						
Guaiacol	2.3	0	.94			
Isoeugenol	0	.28		.57		
Fl	3.8	3.9	.04	.21	5.2	no
BaA	1.5	1.4	.06	.18	3.0	yes
BkF	1.7	1.7	.03	.05	1.7	no
BaP	2.3	2.5	.01	.02	2.0	no
Fifth Experiment, 2/19/93, Borosilicate Well, 6hr duration, .5 hr intervals						
Guaiacol	2.5	0	.44			
Isoeugenol	0	.21		.35		
Fl	.40	.46	.07	.09	1.3	no
BaA	.10	.09	.05	.04	0.8	no
BkF	.23	.25	.01	.04	4.0	yes
BaP	.35	.41	.01	.03	3.0	yes

Figure 1. Apparatus used to prepare, expose to light, and extract organic coated carbon black particles

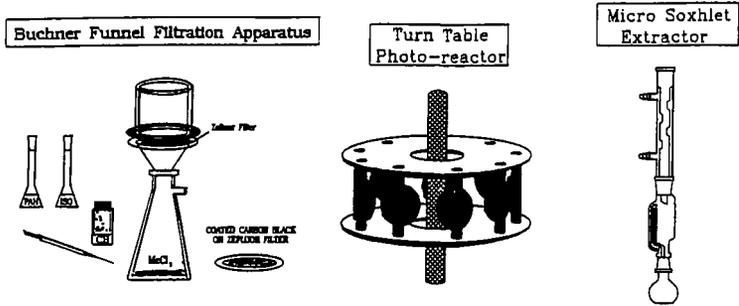


Figure 2. Photodegradation of BaA and BaP coadsorbed with and without isoeugenol on CB, 8/28/92

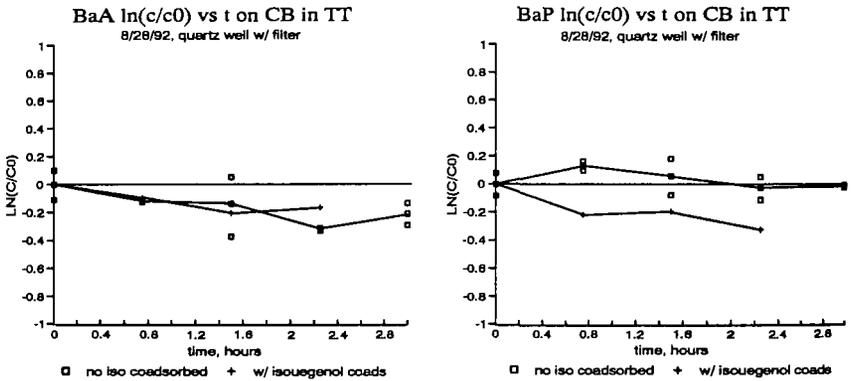
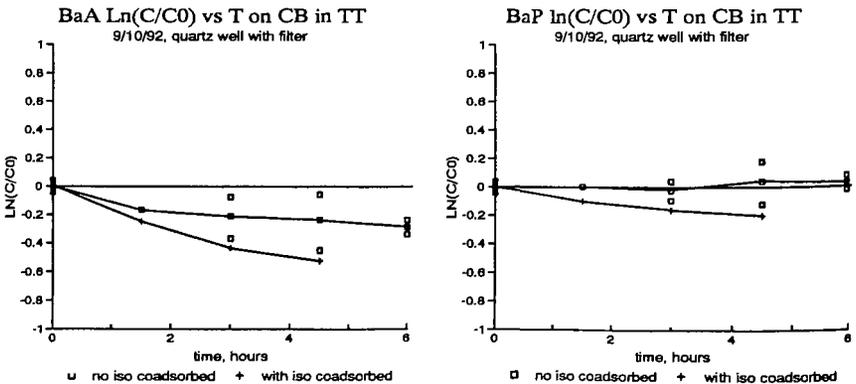


Figure 3. Photodegradation of BaA and BaP coadsorbed with and without isoeugenol on CB, 9/10/92



# Mechanistic and Kinetic Studies of the Photodegradation of Benz(a)anthracene in the Presence of Methoxyphenols

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*Abstract - Kinetic studies were employed to assess an empirical rate law describing the rate of photodegradation of polycyclic aromatic hydrocarbons (PAH) in the presence of substituted methoxyphenols. A solution of benz(a)anthracene (BaA) and vanillin in toluene was chosen as the model system. A rate law and corresponding rate constants were determined for this system:  $d[BaA]/dt = k_A[BaA] + k_B[BaA][Vanillin]$ , where  $k_A = 0.024 \pm 0.005 \text{ hr}^{-1}$  and  $k_B = 81.17 \pm 3.19 \text{ M}^{-1} \text{ hr}^{-1}$ . Further experiments using structure-reactivity relationships were applied to the model system to investigate the mechanism for BaA photodegradation. Data from these experiments suggest that the rate determining step in the mechanism is hydrogen abstraction of the phenolic hydrogen from vanillin.*

## Introduction

Photochemical reaction is an important removal process for atmospheric polycyclic aromatic hydrocarbons (PAH).<sup>1,2</sup> PAH photochemical reactivity in organic solvents has been studied extensively for over 40 years, and singlet oxygen has been determined as the most important oxidant.<sup>3-6</sup> There has also been a considerable amount of research conducted on gas-phase PAH photoreactivity, and it is known that hydroxyl attack is the major oxidation pathway.<sup>7,8</sup> However many of the most mutagenic PAH in the atmosphere are primarily associated with atmospheric particulate matter.<sup>9</sup> PAH associated with combustion source particles are also photochemically reactive,<sup>10,11</sup> but there has been very little work done in determining mechanisms of photodegradation for particulate bound PAH because information on particle composition is generally incomplete and varies considerably from source to source.

Reported photolysis rates for particulate bound PAH vary widely.<sup>12-14</sup> It has been suggested that one reason such variations exist is that the rates are strongly influenced by the chemical and physical surface properties of the associated particles.<sup>15</sup> These properties vary significantly depending on the source, fuel, and combustion conditions under which the particles are generated. For example, 30-60% of the carbon associated with diesel soot is elemental.<sup>16</sup> The rest is comprised mostly of nonpolar aliphatic and aromatic organics.<sup>17</sup> In contrast, as much as 90% of the carbon associated with wood smoke particles is organic.<sup>18</sup> This organic carbon is much more polar than that associated with diesel soot and contains large amounts (120-300ug/mg of particulate carbon) of methoxylated phenols.<sup>19</sup> Wood soot particles also form a viscous liquid when collected by impaction and it has been suggested that PAH might be dissolved in a liquid layer comprised of these organics on the particle.<sup>20,21</sup>

It was previously reported by members of this group<sup>20</sup> that methoxyphenols greatly enhance the photodegradation of PAH in solution. Thus, since methoxyphenols comprise such a large fraction of the organic material associated with wood smoke<sup>19</sup>, it seems reasonable that they may participate in the degradation of PAH associated with wood soot. This is in contrast to previous ideas that suggest that particulate PAH degradation is due solely to reaction with gasphase oxidants or simple photolysis. Therefore, it is desirable to try to gain an understanding of the mechanism by which methoxyphenols participate in this reaction and to formulate a method to obtain a rate law and rate constants for several PAH and methoxyphenols. In this paper we will discuss the experiments used to develop this methodology and present a rate law, rate constants, and possible mechanism for a model system--benz(a)anthracene and vanillin in a toluene solution.

## Experimental Section

All photodegradation experiments were carried out in a merry-go-round reactor (Ace Glassware, Vineland, NJ) equipped with a 450 W medium pressure mercury arc lamp in a quartz immersion well and a 366nm filter. The entire apparatus was submerged in a 18 gal waterbath that was maintained at a constant temperature of  $16.5 \pm 0.5^\circ\text{C}$  by pumping the water (flow rate = 75ml/min) through exterior copper coils that were submerged in a 20 gal ice bath. Samples were irradiated in 13mm x 100mm quartz test tubes (Ace Glassware). Light intensity was periodically measured with a ferrioxalate actinometer,<sup>20</sup> and averaged around  $2.2 \pm 0.3 \times 10^{16}$  photons/sec.

All quantitative analysis was conducted on a Hewlett-Packard 5890 gas chromatograph (GC) equipped with a J&W, 30 m, 0.32 mm i.d., DB-5 column with a 0.25 um film thickness and interfaced to a Hewlett-Packard 5971A Mass Selective Detector. All injections were performed on column, and the acquisition mode was selected ion monitoring. The temperature program was:  $110^\circ\text{C}$  for 2 min,  $110\text{-}220^\circ\text{C}$  at  $12^\circ\text{C}/\text{min}$ ,  $220\text{-}270^\circ\text{C}$  at  $6^\circ\text{C}/\text{min}$ ,  $270\text{-}300^\circ\text{C}$  at  $20^\circ\text{C}/\text{min}$ , hold at  $300^\circ\text{C}$  for 1 min.

Experiments designed to assess structure-reactivity relationships were performed by preparing four sets of samples simultaneously. Each set consisted of four samples and one standard. All solutions were prepared in optima grade toluene (Fisher T291-4). The concentration of benz(a)anthracene (Aldrich B220-9) in all sets was  $1 \times 10^{-5}$  M. The final volume of

each samples was 5 ml. Each set contained a different para-substituted guaiacol. Set 1 contained  $1 \times 10^{-3}$  M acetovanillone (Aldrich A1,080-9). Set 2 contained  $1 \times 10^{-3}$  M 4-hydroxy-3-methoxy benzonitrile (Aldrich 16,260-4). Set 3 contained  $2 \times 10^{-4}$  M 4-nitroguaiacol (Aldrich 32,682-8). Set 4 contained  $1 \times 10^{-3}$  M vanillin (Aldrich V110-4). Four 5 ml samples from each set were irradiated simultaneously. The rate of decay of BaA was monitored by removing one sample from each set from the reactor every hour for four hours and quantitating on the GC/MSD.

Rate law experiments were conducted by preparing four sets of samples simultaneously. All solutions were prepared in optima grade toluene. The concentration of BaA in all samples was  $1 \times 10^{-5}$  M. The concentration of vanillin in set 1 was  $2 \times 10^{-3}$  M, in set 2 was  $1 \times 10^{-3}$  M, in set 3 was  $5 \times 10^{-4}$  M, and in set 4 was  $2 \times 10^{-4}$  M. The rate of decay of BaA was monitored by removing one sample from each set from the reactor every hour for four hours and quantitating on the GC/MSD.

## Results and Discussion

It was previously determined by this group<sup>20</sup> that the photodegradation of BaA exhibits pseudo-first order rate behavior when samples are flooded with vanillin (i.e. concentration of vanillin is at least 20 times higher than the concentration of BaA). The rate law that describes this behavior is:

$$d[\text{BaA}]/dt = k_{\text{obs}}[\text{BaA}]$$

To elucidate the form of  $k_{\text{obs}}$ , an experiment was performed to examine the relationship between vanillin concentration and  $k_{\text{obs}}$ . Four sets of samples, each flooded with a different amount of vanillin, were irradiated in the photoreactor simultaneously. The data is listed in Table I.

TABLE I. Correlation between Vanillin Concentration and  $k_{\text{obs}}$

SET #	[Vanillin] (M)	[BaA] (M)	$k_{\text{obs}}$ ( $\text{hr}^{-1}$ )
1	$2 \times 10^{-3}$	$1 \times 10^{-5}$	$0.176 \pm 0.017$
2	$1 \times 10^{-3}$	$1 \times 10^{-5}$	$0.097 \pm 0.003$
3	$5 \times 10^{-4}$	$1 \times 10^{-5}$	$0.058 \pm 0.006$
4	$2 \times 10^{-4}$	$1 \times 10^{-5}$	$0.044 \pm 0.004$

A plot of  $k_{\text{obs}}$  versus vanillin concentration gives a straight line ( $r^2=0.995$ ) with a slope of  $81.17 \pm 3.19 \text{ M}^{-1} \text{ hr}^{-1}$  and a y-intercept of  $0.024 \pm 0.005 \text{ hr}^{-1}$  (Figure 1). Since this plot yields a straight line with a positive intercept, the rate equation for BaA photodegradation in the presence of vanillin is:

$$d[\text{BaA}]/dt = k_A[\text{BaA}] + k_B[\text{BaA}][\text{Vanillin}]$$

where  $k_A = y\text{-intercept}$  and  $k_B = \text{slope}$ . This type of treatment requires that vanillin concentration be relatively constant over the course of the experiment. In all four sets vanillin degradation was less than 15%.

The form of this rate law implies that there are at least two mechanisms responsible for BaA photodegradation in this system. The ratio of the rate constants suggests that the mechanism involving vanillin does not influence the overall rate unless the concentration of vanillin exceeds  $3 \times 10^{-5}$  M (5 ng/ $\mu\text{l}$ ). At vanillin concentrations above  $3 \times 10^{-3}$  M (500 ng/ $\mu\text{l}$ ), the vanillin dependent mechanism becomes the only important pathway for BaA degradation. Considering that PAH are known sensitizers of singlet oxygen and that attack of singlet oxygen is the major photodegradation pathway for PAH in organic solvents<sup>3-6</sup>, it seems reasonable to assume that the term independent of vanillin concentration is due to singlet oxygen attack on BaA. Furthermore, benz(a)anthracene-7,12 dione, which is a known product of singlet oxygen addition to BaA, has been identified as a reaction product by matching its mass spectrum to a standard. However a singlet oxygen mechanism of this type generally produces second order kinetics.<sup>3-6</sup> Thus further study is needed to confirm the mechanism that is responsible for the first term in the rate law. It is interesting to note that Hawthorne et al<sup>22</sup> have observed the phototoxidation of isoeugenol to vanillin on wood soot particles. This process occurs by singlet oxygen oxidation in solution.<sup>23</sup> Thus perhaps singlet oxygen oxidation is occurring in the organic liquid layer on wood soot particles despite its insignificant contribution as a gas-phase oxidant.

Given the above rate expression, an attempt was made to determine the mechanism responsible for the second term in the rate law. In 1972, T. Matsuura documented that triplet sensitizers were capable of abstracting phenolic hydrogen from catechol and hydroquinone derivatives.<sup>23</sup> This precedence suggested that in our model system BaA may be acting as a triplet sensitizer and abstracting the phenolic hydrogen of vanillin to create a phenoxy radical. Bordwell and Cheng<sup>25</sup> showed that electron donating and electron withdrawing para-substituents were able to stabilize phenoxy radicals. They found that a linear free energy relationship existed between the stabilizing effects of electron donating substituents and

their  $\sigma^+$  parameters. The  $\sigma^+$  parameters are defined as the log of the ratio of the acid dissociation constants for different para substituted t-cumyl chlorides to the acid dissociation constant for unsubstituted t-cumyl chloride. They are a measure of a substituent's ability to stabilize an electron deficient reaction site, that is para to the substituent, by coming into direct, through resonance with the reaction site. The relationship that Bordwell and Cheng found suggest that  $\sigma^+$  parameters are measure of phenoxy radicals stability. Thus in order to determine if BaA was abstracting hydrogen from vanillin to create phenoxy radicals, an experiment was performed to see if BaA rates of photodegradation in various para-substituted methoxyphenols could be correlated with the  $\sigma$  parameters corresponding to those para-substituents. However in this case, electron withdrawing substituents were used instead of electron donating substituents. So  $\sigma^-$  parameters were used instead of  $\sigma^+$  because  $\sigma^-$  parameters are a measure of an electron withdrawing para-substituent's ability to come into direct, through resonance with a para-reaction site.

Four different sets of samples were irradiated in the photoreactor simultaneously. Each set contained BaA and a different para-substituted guaiacol. A rate constant ( $k_B$ ) was obtained for each set. The data is listed in table 2.

**TABLE 2. Correlation between BaA Photodegradation in the Presence of Various Para-substituted Methoxyphenols and the  $\sigma^-$  Parameters Corresponding to those Para-substituents.**

SET #	Methoxyphenol	$\sigma^-$	$k_B$ ( $\text{hr}^{-1}$ )
1	Acetovanillone	0.84	$0.043 \pm 0.006$
2	4-hydroxy-3-methoxy benzonitrile	0.88	$0.032 \pm 0.003$
3	4-nitroguaiacol	1.24	$0.465 \pm 0.025$
4	Vanillin	1.03	$0.083 \pm 0.006$

A Hammett style plot of  $\log(k_B)$  versus the  $\sigma^-$  parameters corresponding to the para-substituted groups yields a straight line ( $r^2 = 0.96$ ) (Figure 2). The  $\sigma^-$  parameters seem to be a relative gauge of the amount of stability that the corresponding para-substituents yield to a phenoxy radical. For example,  $\text{NO}_2$  has a relatively high  $\sigma^-$  parameter ( $\sigma^- = 1.24$ ). This is due to its strong ability to delocalize the odd electron in the corresponding phenoxy radical by coming into direct resonance with the reaction site (Figure 3). This delocalization stabilizes the radical product and thus decreases the free energy of the reaction compared to that of an unsubstituted guaiacol. This decrease in free energy is related to the rate through the Hammett equation:

$$\Delta G_{\text{NO}_2}^\ddagger - \Delta G_{\text{H}}^\ddagger = -2.303RT\sigma^-$$

$$\sigma^- = \log(k_{\text{NO}_2} / k_{\text{H}})$$

where  $\Delta G^\ddagger$  is the free energy difference between the ground state complex and the transition state,  $k_{\text{NO}_2}$  and  $k_{\text{H}}$  are the second order rate constants for BaA photodegradation (i.e.  $k_B$ ) in the presence of 4-nitroguaiacol and guaiacol respectively,  $R$  is the ideal gas constant, and  $T$  is the temperature. This type of relationship shows that the rate increases with  $\sigma^-$ . As stated earlier, Bordwell and Cheng observed<sup>24</sup> that a correlation existed between phenoxy radical stability and  $\sigma^+$  parameters corresponding to electron donating para-substituents. Thus whether a group is electron donating or electron withdrawing does not seem to be the important factor in the stabilization of these radicals. It is the relative ability of the group to come into direct resonance with the reaction site and delocalize the odd electron that seems to exert the largest influence on the phenoxy radical stability. Therefore it seems that the most likely interpretation of the linearity of the Hammett plot is that hydrogen abstraction of the phenolic hydrogen of vanillin is the rate determining step of the mechanism.

A mechanism in which triplet BaA abstracts the phenolic hydrogen of vanillin is shown in Figure 4. In this mechanism,  $k_1$  is a term relating light intensity to the total light that is absorbed in the reaction cell. It is not actually a constant because it depends on both BaA and vanillin concentrations. Yet as long as vanillin concentration is kept below  $5 \times 10^{-3}$  M and BaA concentration is kept below  $5 \times 10^{-5}$  M, this term is only weakly dependent on concentration and thus is essentially constant. This was the case for all experiments conducted in this study. The average value of  $k_1$  was approximately 2.2 and varied less than 5% over the course of any experiment. The term  $\phi_{\text{isc}}$  is the quantum yield for inter-system crossing and  $I_0$  is the light intensity at 366nm. The constants  $k_2$  and  $k_3$  represent the rate of triplet excitation and the rate of hydrogen abstraction respectively.

The rate law for this mechanism is also shown in Figure 4. This mechanism can be easily fit to the observed rate law. The only assumption that is needed is  $k_2 \gg k_3[\text{Van}]$ . By substituting in values for  $I_0$ ,  $\epsilon^{\text{BaA}}$ ,  $\phi_{\text{isc}}$ ,  $k_1$ , and  $k_B$ , a value of  $0.4\text{M}^{-1}$  is obtained for the ratio of  $k_2/k_3$ . Thus for the vanillin concentrations used in this study (i.e.  $< 2 \times 10^{-3}\text{M}$ ),  $k_2$  is much larger than  $k_3[\text{Van}]$ . The value used here for  $\phi_{\text{isc}}$  is for BaA in pure benzene and is assumed to be very similar to what it would be in toluene. The variance is surely less than an order of magnitude. So, the assumption needed to make the proposed mechanism fit the observed rate law is valid.

### Summary and Conclusions

The findings of this study suggest that the mechanism by which BaA photodegrades in the presence of vanillin is by hydrogen abstraction of the phenolic hydrogen of vanillin by excited triplet BaA. The mechanism proposed can be easily fit to the observed rate law. Thus these findings suggest that if PAH are actually dissolved in an organic layer that contains large amounts of methoxyphenols on wood soot particles, then the model system used in this study may be directly applicable to PAH photodegradation on wood soot particles. If rate constants were obtained for several PAH and methoxyphenols using the methodology set out in this study, then modeling the atmospheric fate of PAH associated with wood soot particles would be possible. The rates in solution will obviously be different from those on wood soot. The quantum yield for inter-system crossing ( $\phi_{\text{isc}}$ ) and the rate of triplet de-excitation ( $k_2$ ) are both medium dependent. Furthermore, if the organic layer on wood soot particles is extremely viscous then the rate of hydrogen abstraction ( $k_3$ ) may be diffusion controlled. This diffusion controlled rate would be temperature dependent and this dependence would have to be taken into account. Yet despite these differences, if the mechanism responsible for PAH photodegradation on wood soot particles is known then it would be possible to model their behavior.

This study suggests that further research on heterogeneous reactions in the atmosphere should be conducted and that particular attention be applied to the chemical composition of combustion aerosols.

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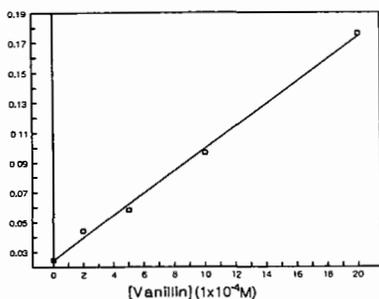


Figure 1: Correlation of Observed Rate Constant with Vanillin Concentration

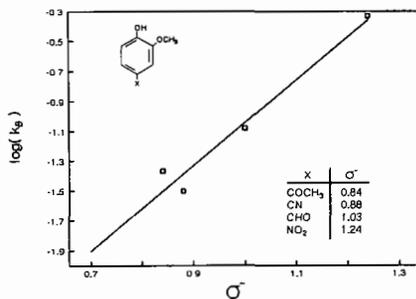


Figure 2: Hammett Plot for p-Substituted Guaiacols

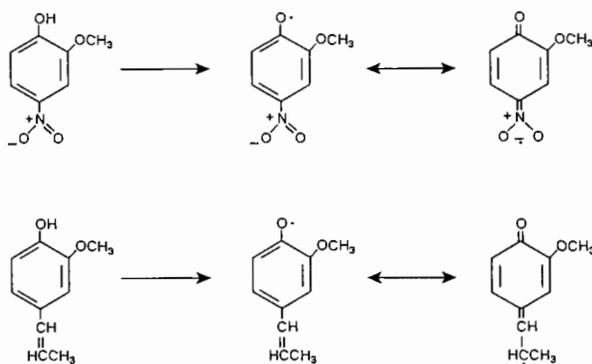
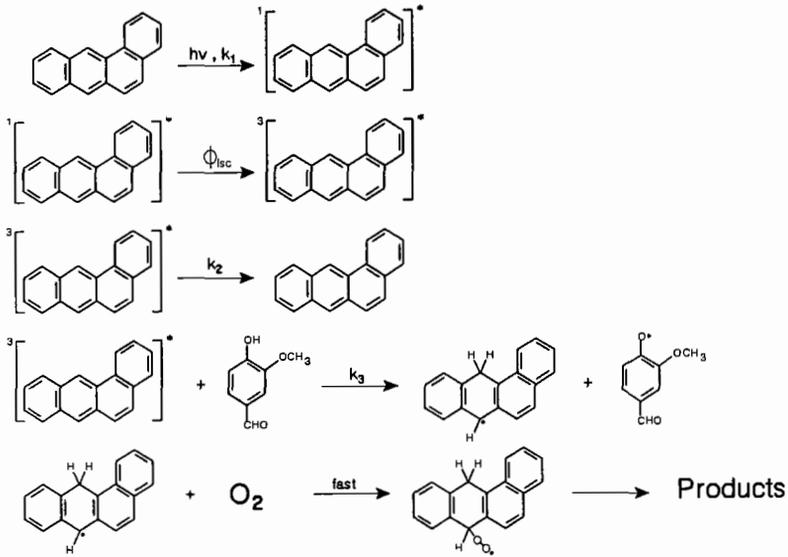


Figure 3: Resonance Stabilization of Phenoxy Radicals by Electron Withdrawing (NO<sub>2</sub>) and Electron Donating Groups (HC=CHCH<sub>3</sub>)

Figure 4: Hydrogen Abstraction Mechanism



$$\text{Rate} = k_3 [{}^3\text{BaA}^*][\text{Van}]$$

$$\text{Rate} = k_3 [\text{Van}] \left[ \frac{\Phi_{isc} [{}^1\text{BaA}^*]}{k_2 + k_3 [\text{Van}]} \right]$$

$$\text{Rate} = k_3 [\text{Van}] \left[ \frac{I_0 \epsilon_{300}^{\text{BaA}} \Phi_{isc} k_1 [\text{BaA}]}{k_2 + k_3 [\text{Van}]} \right]$$

$$\text{where } k_1 = \frac{1 - 10^{-\epsilon_{300}^{\text{BaA}} [\text{BaA}] - \epsilon_{300}^{\text{Van}} [\text{Van}]}}{\epsilon_{300}^{\text{BaA}} [\text{BaA}] + \epsilon_{300}^{\text{Van}} [\text{Van}]}$$

if  $k_2 \gg k_3 [\text{Van}]$

$$\frac{-d[\text{BaA}]}{dt} = k_B [\text{BaA}][\text{Van}] \quad \text{where } k_B = \frac{k_3 I_0 \epsilon_{300}^{\text{BaA}} \Phi_{isc} k_1}{k_2}$$

*Session 4*  
*Measurement and Monitoring*  
*of Toxics, O<sub>3</sub> and PAN*

## **Requirements For The Establishment Of Enhanced Ozone Monitoring Networks**

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### **ABSTRACT**

In accordance with the Clean Air Act Amendments of 1990, the Environmental Protection Agency (EPA) has developed rules for the establishment of enhanced ozone monitoring networks, or Photochemical Assessment Monitoring Stations (PAMS), in ozone nonattainment areas designated as serious, severe, and extreme. These stations will collect ambient air measurements for a target list of volatile organic compounds (VOC) including several carbonyls, and oxides of nitrogen ( $\text{NO}$ ,  $\text{NO}_2$ , and  $\text{NO}_x$ ), ozone, and both surface and upper air meteorological measurements.

EPA anticipates that the data produced by the PAMS will enhance the ability of the State and Local air pollution control agencies to identify and respond to ozone nonattainment conditions by developing and implementing responsible, cost-effective ozone control strategies. Further, the Agency anticipates that the measurements will be highly valuable in verifying emission inventories and corroborating area-wide emissions reductions. The data will be used to evaluate, adjust, and provide input to the photochemical grid models utilized by the States to develop and demonstrate the success of their control strategies. The PAMS will provide constructive information for the evaluation of population exposure and the development of ambient ozone and ozone precursor trends. This paper will examine the regulatory requirements of the rules and the implications for implementation.

## INTRODUCTION

On March 4, 1992, the Environmental Protection Agency proposed amendments to the ambient air quality surveillance rules (40 CFR Part 58) to provide for the enhanced monitoring of ozone and oxides of nitrogen and for the additional monitoring of volatile organic compounds (including carbonyls) to comply with the requirements of Title I, Section 182 of the Clean Air Act Amendments of 1990. These proposed modifications were proffered to obtain more comprehensive and representative data on ozone air pollution. Subsequently, following an extended public comment period, on February 12, 1993, the final rules were promulgated in the *Federal Register* (58 FR 8452). These regulations require the affected States to adopt and implement a program to improve ambient monitoring activities and the monitoring of emissions of oxides of nitrogen and volatile organic compounds and require States to establish Photochemical Assessment Monitoring Stations (PAMS) as part of their SIP monitoring networks in ozone nonattainment areas classified as serious, severe, or extreme. Additionally, each State implementation plan (SIP) for the affected areas must be amended to include provisions for such ambient monitoring. The principle reasons for requiring the collection of additional ambient air pollutant and meteorological data are, primarily, the historical challenges faced by the State and Local Government air pollution control agencies in attaining the National Ambient Air Quality Standards (NAAQS) for ozone nationwide, and secondly, the need for a more comprehensive air quality database for ozone and its precursors to explain the effects of ozone control strategies.

## PROGRAM OBJECTIVES

In formulating the PAMS program, EPA has endeavored to provide a sensible balance between the costs of the program and the degree to which the program objectives are satisfied. The Agency has maintained that in formulating the data requirements for the PAMS program, it was necessary to accept some compromises, (i.e., some more crucial objectives would be better satisfied than other less important objectives). EPA is committed to requiring a program which would comprise the best technical-fiscal stability to maximize the utility of a variety of program objectives. EPA has only provided the framework for a minimum required monitoring strategy; States are encouraged to implement larger, more comprehensive networks if those networks will provide a superior or equivalent database for the fulfillment of the program objectives.

The primary objective of the enhanced ozone monitoring revisions is to provide an air quality data base that will assist air pollution control agencies in evaluating, tracking the progress of, and, if necessary, refining control strategies for attaining the ozone National Ambient Air Quality Standard (NAAQS). Ambient concentrations of ozone and ozone precursors will be used to make attainment/nonattainment decisions, aid in tracking VOC and NO<sub>x</sub> emission inventory reductions, better characterize the nature and extent of the ozone problem, and prepare assessments of air quality trends. In addition, data from the PAMS will provide an improved data base for evaluating photochemical model performance, especially for future control strategy mid-course corrections as part of the continuing air quality management process. The data will be particularly useful to States in ensuring the implementation of the most cost-effective regulatory controls.

Specific provisions of the rule require the establishment and operation of up to 5 PAMS stations in each affected Metropolitan Statistical Area or Consolidated Metropolitan Statistical Area (MSA/CMSA), depending on the population of the area (See Figure 1). Those stations are identified by number and defined as follows:

- o Site #1 - These sites are established to characterize upwind background and transported ozone/precursor concentrations entering the area and will identify those areas which are subjected to incoming transport of ozone. The #1 Sites are located in the predominant morning upwind direction from the local area of maximum precursor emissions and at a distance sufficient to obtain urban scale measurements. Typically, these sites will be located near the upwind edge of the photochemical grid model domain.
- o Site #2 - These sites are established to monitor the magnitude and type of precursor emissions in the zone where maximum precursor emissions are expected to impact and are suited for the monitoring of urban air toxic pollutants. The #2 Sites are located immediately downwind (using the same morning wind direction for locating Site #1) of the area of maximum precursor emissions and are typically placed near the downwind boundary of the central business district to obtain neighborhood scale measurements representative of the MSA/CMSA. Additionally, a second #2 Site may be required depending on the size of the area, and should then be placed in the second-most predominant morning wind direction.

- o **Site #3** - These sites are intended to monitor maximum ozone concentrations occurring downwind from the area of maximum precursor emissions. Locations for #3 Sites should be chosen so that urban scale measurements are obtained. Typically, these sites are located 10 to 30 miles downwind from the fringe of the urban area.
- o **Site #4** - These sites are established to characterize the extreme downwind transported ozone and its precursor concentrations exiting the area and will identify those areas which are potentially contributing to ozone transport into other areas. The #4 Sites are located in the predominant afternoon downwind direction from the local area of maximum precursor emissions at a distance sufficient to obtain urban scale measurements. Typically, these sites will be located near the downwind edge of the photochemical grid model domain.

Each station will sample for speciated volatile organic compounds (VOC), often including several carbonyls, and ozone, oxides of nitrogen, and surface (10-meter) meteorological parameters; the network requirements vary somewhat with the size of the MSA/CMSA (See Figure 2). Additionally, each area must monitor upper air meteorology at one representative site. The rule allows a 5-year transition or phase-in schedule for the program at a rate of at least one station per area per year. Further, the rule provides for the submission and approval of alternative network designs and sampling schemes. Such alternative mechanisms for compliance with the rules are especially valuable to States which are currently engaged in some different form of ozone precursor monitoring which has proved adequate for their SIP needs.

Specific and often different monitoring objectives are associated with each specific PAMS monitoring location. These monitoring objectives can be summarized into categories to support the following activities: control strategies, photochemical modeling, emissions inventories, trends, attainment/nonattainment decisions, and exposure analyses. A monitoring network which adequately supports these six objectives will provide the initial stepping stones that constitute a pathway toward attainment of the National Ambient Air Quality Standard (NAAQS) for ozone.

**Objective #1: Provide a speciated ambient air data base which is both representative and useful for ascertaining ambient profiles and distinguishing among various individual VOC.**

A fundamental objective of the enhanced ozone and ozone precursor monitoring regulations is to provide a mechanism whereby air pollution control agencies can obtain an air quality database that will assist in evaluating, tracking the progress of, and, if necessary, refining control strategies for attaining the ozone NAAQS. This comprehensive data base will allow the States to focus their control strategies where they will be the most beneficial to attain the NAAQS and to re-evaluate their existing ozone control programs. These PAMS data, especially those collected at Sites #1 and #2, will enhance the characterization of ozone concentrations and provide critical information on the precursors which cause ozone. Speciation of measured VOC data and additional NO<sub>x</sub> data are expected to allow the determination of which species are most affected by local emissions reductions and assist in developing cost-effective, selective VOC and/or NO<sub>x</sub> reductions and control strategies.

**Objective #2: Provide local, current meteorological and ambient data to serve as initial and boundary condition information for photochemical grid models.**

The PAMS network requirements are tailored to provide specific data measurements which can be utilized by photochemical modelers to refine their estimates of initial and boundary conditions, provide a means to evaluate the predictive capability of the models, and minimize the available adjustment of model inputs. Such information will tend to increase the probability that the model's calculations will reflect the "right answer for the right reason" rather than the "right answer for the wrong reason" and reduce the uncertainties associated with estimated model inputs. In fact, the upwind site (Site #1) and the downwind site (Site #4) are located so as to quantify the atmospheric conditions at the upwind and downwind extremes of the photochemical modeling domain.

Heretofore, the national air pollution control program has not had the benefit of comprehensive ozone precursor data as a tool for evaluating, calibrating, performing diagnostics, or otherwise adjusting and conducting reality checks on the operation of the Urban Airshed Model (UAM). EPA views the PAMS networks as vital steps forward in complementing grid model applications.

**Objective #3: Provide a representative, speciated ambient air data base which is characteristic of source emission impacts.**

The emissions inventory serves as an essential element of the air management process as well as a fundamental input for photochemical models. Verification of reported emissions and the tracking of changes in the atmospheric VOC profiles can assist in the evaluation of control strategy effectiveness. Given that the emissions inventory is the foundation building block for the entire SIP development process, it is critical that its accuracy be optimized. While the regulatory assessments of progress will be made in terms of emission inventory estimates, the ambient data can provide independent trends analyses and corroboration of these assessments which either verify or highlight possible errors in emissions trends indicated by the inventories. The ambient assessments, using speciated data, can gauge the accuracy of estimated changes in emissions. The speciated data can also be used to assess the quality of the speciated VOC and NO<sub>x</sub> emission inventories. Utilizing other computer modeling techniques, PAMS data will help resolve the roles of transported and locally emitted ozone precursors in producing an observed exceedance and may be utilized to identify specific sources emitting excessive amounts of precursors.

**Objective #4: Provide ambient data measurements which would allow later preparation of pollutant trends assessments.**

Long-term PAMS data will be used to assess ambient trends for speciated VOC, NO<sub>x</sub>, and in a more limited way, for toxic air pollutants. Multiple statistical indicators will be tracked, including ozone and its precursors during the events encompassing the days during each year with the highest ozone concentrations, the seasonal means for these pollutants, and the annual means at representative locations. The more PAMS that are established in and near nonattainment areas, the more effective the trends data will become. Note, however, that in general it will only be appropriate to combine data from like sites; therefore, trends will likely need to be constructed on a site-by-site or combination-of-like-sites basis. As the spatial distribution and number of ozone and precursor monitors grows, trends analyses will be less influenced by instrument or site location anomalies. The requirement that surface meteorological monitoring be established at each PAMS will help maximize the utility of these trends analyses by comparisons with meteorological trends, and transport influences.

**Objective #5: Provide additional measurements of selected criteria pollutants.**

Like SLAMS and NAMS data, PAMS data will be used for monitoring ozone exceedances and providing input for attainment/nonattainment decisions. Additionally, the NO<sub>x</sub> data can be utilized to augment monitoring for compliance with the NAAQS for NO<sub>2</sub> where such data is gathered with the Federal Reference Method (FRM) and is taken on a year-round basis. Ultimately, the success of any air pollution control strategy is appraised by its ability to achieve compliance with the NAAQS. (Note that the PAMS will expand the spatial coverage of NAAQS-related monitoring.) Although the data at any PAMS site can be used for these purposes, it is expected that Site #3 will constitute the maximum ozone concentration site for comparison with the NAAQS. Further, the additional data will provide an expanded foundation for developing and administering maintenance plans required by the Clean Air Act.

**Objective #6: Provide additional measurements of selected criteria and non-criteria pollutants from properly-sited locations.**

PAMS data can be used to better characterize ozone and toxic air pollutant exposure to populations living in serious, severe, or extreme areas. Annual mean toxic air pollutant concentrations can be calculated to aid in estimating the average exposure to the population associated with individual VOC species, which are considered toxic, in urban environments. Specifically, by measuring the VOC targeted by PAMS, a number of toxic air pollutants will also be measured. Although compliance with Title I, Section 182 of the Clean Air Act Amendments does not require the measurement and analysis of additional toxic air pollutants, the Agency believes that the PAMS stations can serve as cost-effective platforms for a limited enhanced air toxics monitoring program. The adjunct use of PAMS for air toxics monitoring will allow the consideration of air toxics impacts in the development of future ozone control strategies. The establishment of a second PAMS Site #2 in an MSA/CMSA will provide an even better data base for such uses. Both Sites #2 and #3 will probably be the best choices for exposure analyses. EPA notes that the PAMS network is not ideal as a source of primary ambient air toxics data and regards the collection of air toxics data as an incidental and secondary, though important, objective of the PAMS system.

## ALTERNATIVE PLANS

During the process of developing the initial proposal for the photochemical assessment monitoring program, EPA noted that each air pollution control agency is subject to its own particular set of problems, strategies, limitations, and authorities. In many cases some of these factors may be sufficiently unique to require tailoring of the PAMS specifications in order to balance the program objectives for a particular geographic area. Accordingly, in the final rule, the Agency incorporated provisions which would allow such tailoring via the development of alternative PAMS monitoring schemes. Such provisions permit alternatives for the number and location of monitoring sites, the sampling/analysis methodology utilized at each site, the frequency of sampling, the specification of wind directions for siting purposes, and the stipulation of the monitoring season. In great part, the approval of alternative plans rests upon the State's ability to provide a balanced response to the program objectives, ensuring a focus on three key elements, i.e., development and evaluation of ozone control strategies, data assistance for photochemical modeling, and tracking of emissions/trends.

Current EPA thinking on alternative plans includes:

- o requiring narrative justification for alternatives with supporting data
- o entertaining optional programs at Sites #1, #3, and #4.
- o establishing higher hurdles for options at Sites #2.
- o requiring submittal of historical sampling data, or
- o requiring side-by-side sampling and analyses

## CONCLUSION

With the promulgation of the PAMS rules, EPA has endeavored to enter a new era of national monitoring management. The program will not only rely on State and Local air pollution control agencies to operate the monitoring systems and report the data, as in the past, but will also encourage innovative thinking in the design, operation, management, and use of proactive monitoring strategies. The Agency believes that PAMS team building will provide both Federal and State/Local government with a forum to produce an environmental data base which will be unequalled in usefulness and quality.

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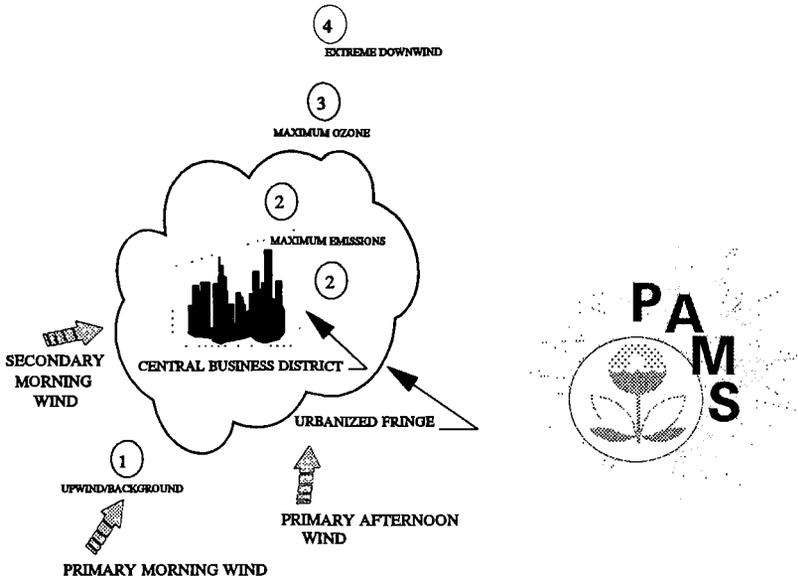


Figure 1. PAMS Network Design

MINIMUM NETWORK REQUIREMENTS		
POPULATION OF MSA/CMSA	FREQ TYPE	SITE LOCATION
LESS THAN 500,000	A or C	(1)
	A/D or C/F	(2)
500,000 TO 1,000,000	A or C	(1)
	B/E	(2)
1,000,000 TO 2,000,000	A or C	(3)
	A or C	(1)
	B/E	(2)
GREATER THAN 2,000,000	B/E	(2)
	A or C	(3)
	A or C	(1)
	A or C	(4)

VOC SAMPLING FREQUENCY REQUIREMENTS	
Type	Requirement
A	8 3-Hour Samples Every Third Day
	1 24-Hour Sample Every Sixth Day
B	8 3-Hour Samples Everyday
	1 24-Hour Sample Every Sixth Day (year-round)
C	8 3-Hour Samples 5 Hi-Event/Previous Days & Every Sixth Day
	1 24-Hour Sample Every Sixth Day

CARBONYL SAMPLING FREQUENCY REQUIREMENTS	
Type	Requirement
D	8 3-Hour Samples Every Third Day
E	8 3-Hour Samples Everyday
F	8 3-Hour Samples 5 Hi-Event/Previous Days & Every Sixth Day

MINIMUM PHASE-IN		
YEARS AFTER PROMULGATION	NUMBER OF SITES OPERATING	OPERATING SITE LOCATION RECOMMENDATION
1	1	2
2	2	2,3
3	3	1,2,3
4	4	1,2,3,4
5	5	1,2,2,3,4

Figure 2. PAMS Network Requirements

**SURVEYS OF THE 189 CAAA HAZARDOUS AIR POLLUTANTS:  
I. ATMOSPHERIC CONCENTRATIONS IN THE U.S.**

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**ABSTRACT**

This paper describes a survey of the ambient air concentrations of the 189 Hazardous Air Pollutants (HAPs) listed in the 1990 Clean Air Act Amendments. The purpose of this survey was to establish typical ranges and average values for HAPs concentrations in the U.S., as a first step in assessing the exposure of the U.S. population to these chemicals. This survey found that the 189 HAPs consist of one group of chemicals frequently measured in many sampling locations, and a second much larger group for which few or no ambient data exist. For 74 chemicals no ambient data were found, and for 45 others fewer than 100 measurements were found. Oxygenated and nitrogenated organics dominate the group for which no data were found; this is probably due to the difficulties in sampling and analyzing for these compounds at ambient levels. For a list of 30 high-priority HAPs, data are more plentiful than for most of the HAPs.

**INTRODUCTION**

To accelerate the pace of identifying and regulating toxic air contaminants, Congress established a list of 189 chemicals designated as Hazardous Air Pollutants (HAPs) in the 1990 Clean Air Act Amendments (CAAA). Those 189 HAPs are a diverse group, including volatile organic compounds (VOCs), polar VOCs, pesticides, semivolatile compounds, and metals. This report presents the results of a survey of ambient concentration data for the 189 HAPs (1). The purposes of this survey are to provide typical data from populated areas of the U.S. with which initial health risk assessments may be done for the 189 HAPs, and to highlight HAPs for which ambient measurements are particularly needed.

**SURVEY PROCEDURES**

The 189 diverse chemicals designated as HAPs were organized into chemical classes to facilitate searching for ambient data. This chemical classification was useful because similar chemicals are frequently measured together, using similar measurement methods. Information on ambient concentrations of the 189 HAPs was located through keyword searches of appropriate computerized databases, in review articles, reference books, proceedings of relevant air-quality conferences, and in unpublished data sets from recent urban air monitoring studies. Ambient concentrations for 70 of the 189 HAPs have been compiled through 1987 in the National VOC Data Base (2,3), and that data base was updated concurrently with the present program (4). For the present study, the ambient data in the 1988 version of the national data base (2,3) were summarized, and were supplemented with ambient data from recent field studies. The search strategy for the 119 HAPs not included in the National VOC Data Base was somewhat different. The 119 HAPs were the subject of computerized and manual searches of the literature to locate ambient data. For each chemical, a keyword search was conducted through the computerized databases of STN International. The databases searched included the Chemical Abstracts (CA) files from 1967 to the present, Chemical Abstracts Previews (CAP) current files, and National Technical Information Service (NTIS) files from 1964 to the present. The search strategy targeted keywords such as "ambient or urban or atmospheric", and "measurements or monitoring or concentration", and "air". The strategy also specifically excluded keywords such as "workplace" or "biological" that were not pertinent to this survey. The search was restricted to English language citations authored in the U.S., in order to focus on data pertinent to toxics exposure of the U.S. population.

The intent of this review was not to catalog every data point or sample, as attempted in the National VOC Database (2,3). Rather, the aim was to compile information on typical concentrations (i.e., mean and/or median), the range of concentrations observed, and the number, locations, and time periods of the measurements. Additional information such as the detection limit of the measurements, the number of results below the detection limit, and the procedure used for calculation of a mean value, was also recorded when available. The focus of this survey was on ambient data in populated (urban to rural) areas of the U.S. To that end, data from remote sites and data indicating direct source sampling were excluded from the survey. In a few cases identification was ambiguous, and scientific judgment was used to exclude data points which were notably higher than the upper range of other data. No effort was made to exclude all measurements that may have been subject to some impact of urban sources, since those data properly represent the upper range of concentrations to which urban residents may be exposed. Efforts were made to assure data quality by selecting from well-documented recent measurements.

The list of 189 HAPs includes some redundant entries, in the form of chemical groups (e.g., xylenes, cresols) and their individual constituent isomers. These chemicals may be used in industrial settings as the mixed isomers, but are generally measured in the atmosphere as individual isomers. Searches were performed for both the individual and mixed isomers, but ambient data were found for only the individual isomers. The HAP denoted as polycyclic organic matter (POM) is comprised of numerous individual compounds, and the compounds measured are not always clearly defined in reports of ambient measurements. For consistency, and to emphasize potential health risks from POM, this survey focused on eight individual POM compounds identified as possible or probable human carcinogens (5,6). Those eight compounds are benzo[a]pyrene, benzo[a]anthracene, dibenzo[a,h]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, indeno[1,2,3-c,d]pyrene, and benzo[g,h,i]perylene. Ambient data were compiled for the sum of these eight POM compounds.

## RESULTS AND DISCUSSION

The results of this survey of ambient concentrations are compiled in a 33-page table, with an associated list of over 80 citations from relevant literature (1). The data table lists all 189 chemicals in the same order as in the CAAA and gives the name and CAS number for each compound, the locations and years of measurements, the number of measurements, the mean, range, and median (if available) of the measured data, the number of the pertinent reference in the associated reference list, and additional comments on the data, such as the number of non-detects. In some cases the number of locations and number of samples were not evident from the literature. In those cases the numbers were estimated. Some studies failed to state the detection limit, or to define the number of measurements below that limit. The value assigned to non-detects (e.g., zero, half the detection limit, etc.) in calculating a mean value was also not often clearly stated. These inconsistencies were addressed by inferring or estimating the detection limits and number of non-detects from information in the literature. Mean values were then calculated assuming half the apparent detection limit for the results below the detection limit.

The most noticeable feature of the data is the wide variation in the amount of data found for individual HAPs. The number of sampling locations varies from zero to over 140, and the number of samples varies from zero to over 10,000. Of particular importance is that the number of samples is zero for 74 of the HAPs, i.e., no ambient data were found. In considering the distribution of the HAPs by number of sampling locations, the greatest frequency is found for zero sampling locations, with the 74 chemicals in this category comprising nearly 40% of the HAPs list. The second largest frequency is for 1-4 sampling locations, again indicating the scarcity of data for some compounds. Only 72 chemicals (38% of the list) show data from at least 5 locations, and only 54 (29%) show data from 10 or more locations.

Figure 1 shows the frequency distribution of HAPs by the number of measurements found, and clearly indicates the wide range in the availability of ambient data for the HAPs. The 74 chemicals for which no ambient data were found constitute the largest frequency range in Figure 1, and a total of 119 chemicals (63% of the list) show less than 100 measurements. However, the second largest frequency range is the 40 chemicals for which over 1,000 measurements were found. This observation illustrates the primary characteristic of the HAPs list from the CAAA: it is a unique mix of some chemicals frequently measured in ambient air, and others rarely or never measured.

It is instructive to explore what types of chemicals predominate among those HAPs for which no ambient data were found. That subject is addressed in Figure 2, which shows the total number of HAPs and the number with no data found, for each of the chemical classes used in the data search. As expected, for classes such as hydrocarbons, aromatic compounds, and their halogenated analogs, data are available for nearly all of the chemicals. These compounds are common toxic, relatively non-polar VOCs, and are readily measured in ambient air by methods such as EPA Compendium Method TO-14. In contrast, no data are available for most of the chemicals in the nitrogenated and oxygenated organic classes. This fact is particularly important because together these two groups comprise half of the HAPs list.

Several reasons may exist for the scarcity of ambient measurements of some chemical classes. For the nitrogenated and oxygenated organics, which collectively fall under the definition of polar VOCs, the most likely reason is the lack of sampling and analysis methods for these compounds. Due to their water solubility and reactivity, measurement of these chemicals at expected ambient levels (ppbv to sub-ppbv) is more difficult than measurement of VOCs, and consequently methods for such chemicals are still in development (7). This survey indicates, therefore, that method development for polar VOCs in air is crucial if measurement and regulation of these HAPs are to be accomplished. For other chemical classes, the scarcity of data in this survey may have other causes. Many chemicals have been measured in the workplace but not in ambient air. For example, the list designates titanium tetrachloride, elemental phosphorus, and dye intermediates such as 3,3'-dimethoxybenzidine as HAPs. Although the potential toxicity of these chemicals has been established, their ambient concentrations have not been measured because they have been considered unlikely to be present at significant concentrations in ambient air. For such compounds, initial ambient measurements focused in areas of known sources may be preferable to widespread survey measurements, in assessing the potential for human exposure to these chemicals.

Another reason for the lack of ambient air data for some HAPs is the ambiguous nature of the identification on the CAAA list. A good example is "coke oven emissions". The emission of a variety of toxic chemicals from coke ovens is well documented, including sulfur compounds, benzene, other aromatics, and polycyclic aromatic compounds. However, it is impossible to quantify those compounds originating in ambient air from coke oven emissions, in the face of other sources of the same compounds, without (e.g.) detailed source apportionment modelling in the area of a coke oven source. As a result, measurements of "coke oven emissions" as a chemical group in urban areas simply do not exist.

The representativeness of the HAPs data for use in health risk assessments is an important issue. Some compounds, such as the chlorinated and aromatic hydrocarbons, have been measured thousands of times in dozens of locations. The geographic spread of the data is also wide, merely because of the large number of studies including these chemicals. Thus it may be argued that sufficient data exist to estimate typical and elevated human exposures to these chemicals. However, as noted above, nearly two-thirds of the 189 HAPs have been measured fewer than 100 times, and a similar number have been measured in fewer than 5 locations. Such small data sets and limited geographic coverage are unlikely to adequately represent the exposure of the U.S. population to those chemicals. More measurements of these compounds are needed if health risk assessment is to be conducted adequately.

As an example of the data compiled in this survey, Table 1 summarizes the most recent data found for a group of 30 high priority HAPs. This list of chemicals was adapted from the draft list of candidate pollutants in the U.S. EPA solicitation for the National Human Exposure Assessment Survey (NHEXAS). The data shown in Table 1 are a subset of the complete data sets compiled for these chemicals in the present study. Shown in the table are the number of study locations, number of samples, mean, range, and years of recent measurements for the 30 chemicals. The availability of data for these key compounds is generally better than for the 189 HAPs as a whole. All of the chemicals in Table 1 have been measured recently in ambient air, and for most of these chemicals several hundred recent samples are indicated. Inspection of the full data set also indicates that the recent data in Table 1 exhibit means and ranges that are generally lower than those of earlier data. This difference may indicate decreases in the emissions of these chemicals. However, changes in the choice of sampling locations may also account for this difference. Site selection in early urban field studies often emphasized worst-case locations such as urban traffic centers; recent studies have tended to emphasize sites that are more representative of local population distributions. As a result, the recent data shown in Table 1 may be useful for initial health risk assessments for these 30 HAPs.

## CONCLUSIONS AND RECOMMENDATIONS

The conclusions of this study are:

1. The 189 HAPs can be divided into two groups: one comprising roughly 30 percent of the list, for which previous ambient measurements have been frequent and widespread, and a second much larger group for which measurements are rare or non-existent.
2. For a core group of key HAPs, recent and earlier ambient data are relatively plentiful, suggesting that initial health risk estimates can be made with the existing data.
3. The major groups of HAPs for which data are lacking are the nitrogenated and oxygenated organics; lack of suitable sampling and analysis methods is the main reason for the lack of data for these chemicals.

The recommendations from this study are:

1. Analytical method development is critically needed for many of the HAPs, particularly for the nitrogenated and oxygenated organics, which collectively may be called polar VOCs.
2. Additional ambient air measurements are needed for at least 70 percent of the HAPs, to improve the representativeness of the data for use in human health risk assessments.
3. Efforts should continue to enlarge the present set of ambient air data for the 189 HAPs. The present survey was not designed to be exhaustive, and inclusion of additional data would be valuable.

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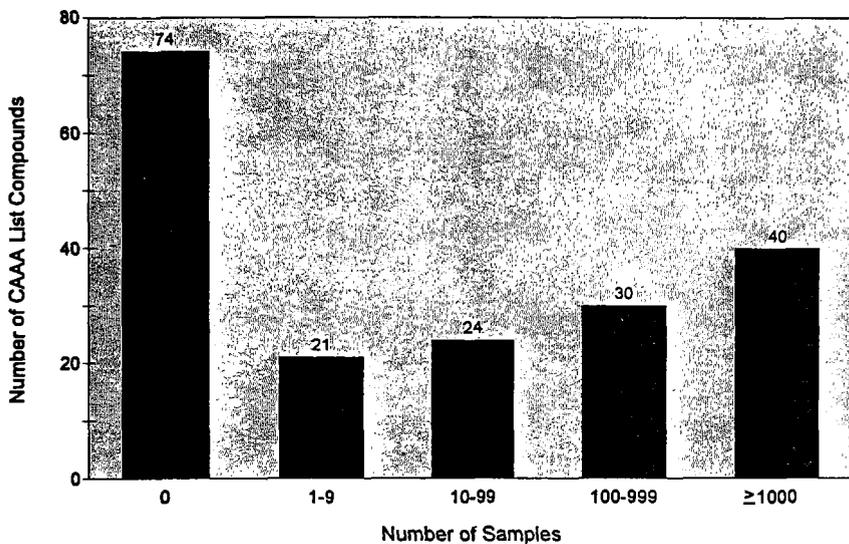


Figure 1. Distribution of the 189 HAPs by Number of Ambient Air Samples

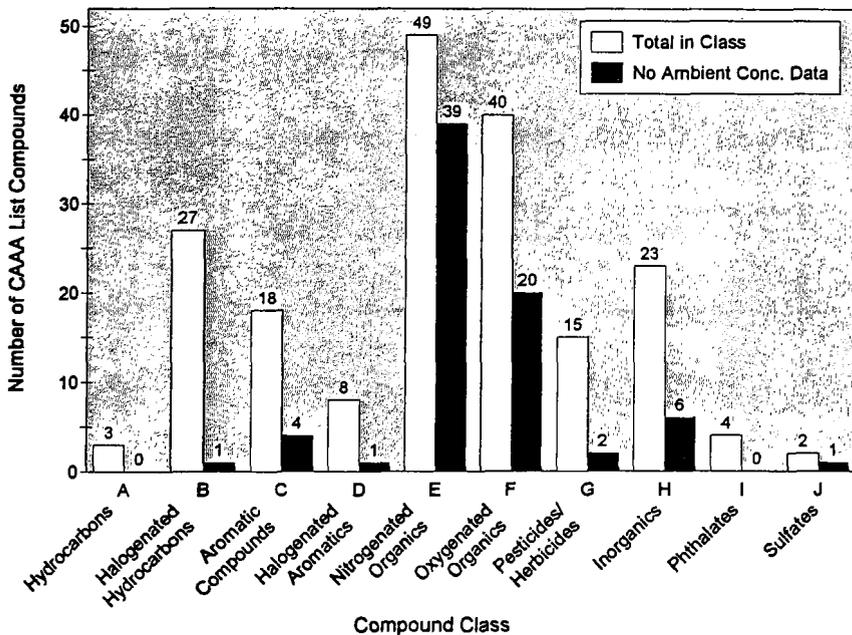


Figure 2. Number of HAPs, and Number for Which No Ambient Data Were Found, for Each of the Chemical Classes Used in the Data Search

TABLE 1. RECENT AMBIENT AIR CONCENTRATIONS DATA FOR 30 HIGH PRIORITY HAPs

No.	Compound	No. of Study Areas	No. of Samples	Overall Mean	Overall Data Range	Study Years
1	Benzene	14	5348	2.8 $\mu\text{g}/\text{m}^3$	<0.05 - 67.3	1989-91
2	Chloroform	13	4368	0.4 $\mu\text{g}/\text{m}^3$	<0.03 - 115	1989-91
3	Formaldehyde	13	804	3.3 $\mu\text{g}/\text{m}^3$	0.12 - 23.4	1989-91
4	Tetrachloroethylene	13	728	3.6 $\mu\text{g}/\text{m}^3$	<0.69 - 104	1989-91
5	1,3-Butadiene	1	349	2.3 $\mu\text{g}/\text{m}^3$	<0.02 - 321	1990
6	Carbon Tetrachloride	13	728	1.2 $\mu\text{g}/\text{m}^3$	<0.06 - 27.8	1989-91
7	Chlorobenzene	13	728	0.12 $\mu\text{g}/\text{m}^3$	<0.09 - 9.1	1989-91
8	Vinylidene Chloride	2	379	ND	<0.12, <0.40 $\mu\text{g}/\text{m}^3$	1989-91
9	Ethylene Oxide	2	>3	<1.8 $\mu\text{g}/\text{m}^3$	0.09 - 1.8	1989
10	Methyl Chloroform	13	728	5.6 $\mu\text{g}/\text{m}^3$	<0.28 - 492	1989-91
11	Methylene Chloride	13	728	2.2 $\mu\text{g}/\text{m}^3$	<0.35-112	1989-91
12	Styrene	3	6117	0.55 $\mu\text{g}/\text{m}^3$	<0.05 - 35.1	1989-91
13	Toluene	14	5348	10.2 $\mu\text{g}/\text{m}^3$	0.11 - 750	1989-91
14	Vinyl Chloride	13	728	0.96 $\mu\text{g}/\text{m}^3$	<0.08 - 202	1989-91
15	Xylenes:					
	o-xylene	3	4999	2.6 $\mu\text{g}/\text{m}^3$	<0.05 - 64.1	1989-91
	m-xylene	3	4999	5.4 $\mu\text{g}/\text{m}^3$	<0.06 - 127	1989-91
	p-xylene <sup>†</sup>	31	785	8.7 $\mu\text{g}/\text{m}^3$	ND - 72	1985-87
16	Lead	2	465	9 $\text{ng}/\text{m}^3$	0.4 - 50	1989-91
17	Arsenic	2	696	2.5 $\text{ng}/\text{m}^3$	1.8 - 7.0	1985, 89
18	Cadmium	1	349	1.2 $\text{ng}/\text{m}^3$	0.3 - 4.1	1985
19	Chromium	3	808	3.3 $\text{ng}/\text{m}^3$	<1 - 30	1985,
20	Mercury	2	178	5.8 $\text{ng}/\text{m}^3$	0.8 - 16	1988-89
21	Nickel	3	664	3.8 $\text{ng}/\text{m}^3$	<2 - 8.7	1985;
22	POMs	7	159	8.4 $\text{ng}/\text{m}^3$	0.3 - 91	1984-91
23	2,3,7,8-TCDD	5	134	0.04 $\text{ng}/\text{m}^3$	Not available	1986-88
24	PCBs	Great Lakes	Many	1.0 $\text{ng}/\text{m}^3$	Not available	Up to 1991
25	Chlordane <sup>†</sup>	2	301	17.1 $\text{ng}/\text{m}^3$	<4 - 628	1987-88
26	2,4-D <sup>†</sup>	2	288	0.003 $\text{ng}/\text{m}^3$	<0.5 - 1.2	1987-88
27	Heptachlor <sup>†</sup>	2	301	7.0 $\text{ng}/\text{m}^3$	<0.5 - 627	1987-88
28	Hexachlorobenzene <sup>†</sup>	2	301	0.04 $\text{ng}/\text{m}^3$	<0.5 - 13.0	1987-88
29	Pentachlorophenol	1	2	0.92 $\text{ng}/\text{m}^3$	0.91-0.92	1989
30	Propoxur <sup>†</sup>	2	301	2.5 $\text{ng}/\text{m}^3$	<3 - 286	1987-88

<sup>†</sup> Mean values calculated using "0" for non-detected samples; all other cases use 0.5xDetection Limit for non-detected samples.

SURVEYS OF THE 189 CAAA HAZARDOUS AIR POLLUTANTS:  
II. ATMOSPHERIC LIFETIMES AND TRANSFORMATION PRODUCTS

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**ABSTRACT**

This paper describes a survey of the atmospheric reactions, products, and lifetimes of the 189 Hazardous Air Pollutants (HAPs) listed in the 1990 Clean Air Act Amendments. This survey focussed on the primary transformation processes for the HAPs, with the aim of identifying toxic reaction products. For 92 of the HAPs, reaction rate, lifetime, and product information were found, including 13 HAPs for which no significant transformation is expected. For 85 other HAPs, rate and lifetime data were found, but no products were identified. For the final 12 HAPs, no reactivity or product data at all were found. Reaction with OH radical is the most common transformation process for the HAPs, with photolysis, deposition, and reactions with ozone, nitrate radicals, and water being generally of secondary importance. The most common HAPs reaction products include low molecular weight aldehydes, alcohols, ketones, organic acids, nitrates, CO, and CO<sub>2</sub>. Some non-toxic chemicals in air may also give HAPs as reaction products.

**INTRODUCTION**

To accelerate the pace of identifying and regulating air contaminants, Congress established a list of 189 chemicals designated as Hazardous Air Pollutants (HAPs) in the 1990 Clean Air Act Amendments (CAAA). Those 189 HAPs are a diverse group, including volatile organic compounds (VOCs), polar VOCs, pesticides, semivolatile compounds, and metals. In addition to the concern of human exposure directly to these 189 chemicals, the CAAA also identifies the need for "consideration of atmospheric transformation and other factors which can elevate public health risks from such pollutants." This survey was performed to identify the primary removal and transformation processes, products, and lifetimes to be expected in the atmospheric degradation of the 189 HAPs.

**SURVEY PROCESS**

For purposes of this survey, the 189 diverse chemicals designated as HAPs were organized into chemical classes to facilitate searching for transformation data. This classification was useful because similar chemicals are frequently evaluated together and are transformed via similar reaction mechanisms. Information on the transformation processes of the 189 HAPs was located using two computerized data bases and through a general review of articles, reference books, proceedings of relevant conferences, and reports. One data base reviewed for reaction rate information was the ABIOTIK<sub>x</sub> software package (1). This program supplied measured reaction rate constants for the degradation of organic compounds in the atmosphere. Also provided were literature citations for the information displayed. If the title of the referenced work implied that reaction products were also identified in the text, then efforts were made to obtain a copy of the manuscript for in-depth review. The second data base employed consisted of a keyword search conducted through the computerized databases of STN International. The databases searched included the Chemical Abstract (CA) files from 1967 to present, Chemical Abstract Preview (CAP) current files, and the National Technical Information Service (NTIS) files from 1964 to present. The search strategy targeted keywords such as "atmospheric or air," "reactions or kinetics or removal," and "rates or constants or lifetime." The search was restricted to English language citations in order to expedite their evaluation. Transformation data were also obtained from published reviews, reference texts, proceedings of meetings, and reports that were not identified during the two database searches. These sources reflected general reference materials available at the time of the survey.

## ATMOSPHERIC LIFETIMES

If the information found for a particular HAP contained rate constants for atmospheric reactions, then an estimated lifetime was computed. For the general case of a chemical (x) reacting with an atmospheric constituent (A), the lifetime ( $\tau$ ) of x was defined as  $\tau_x = 1/kC_A$ , where k is the appropriate rate constant and  $C_A$  is the concentration of A. To perform this calculation, the following assumed concentrations for the major gaseous reactants were used:

Species	Concentration (molecules/cm <sup>3</sup> )
O <sub>3</sub>	1.5 x 10 <sup>12</sup>
OH	3.0 x 10 <sup>6</sup>
NO <sub>3</sub>	2.5 x 10 <sup>9</sup>
HO <sub>2</sub>	1.0 x 10 <sup>9</sup>

These concentrations were meant to represent long-term average concentrations in a relatively polluted environment (2). Photolysis was also included as a transformation pathway. Three lifetime categories were utilized: < 1 day, indicating rapid transformation in the atmosphere; 1-5 days, indicating a more persistent nature; and finally > 5 days, generally indicating that the HAP either reacts slowly or not at all under atmospheric conditions. In some instances, lifetimes indicated in different literature sources for a HAP were not in agreement. To accommodate this, ranges of < 1 to 1-5 days and 1-5 to > 5 days lifetimes were reported. For chemicals which react slowly in the atmosphere, transport and deposition (wet or dry) were included as transformation processes since they determined the limiting lifetime of the HAP. The purpose of this survey was to characterize the dominant features of each HAP's atmospheric transformation, and to document the likely reaction products. The compilation of reaction rate constants, and the detailed evaluation of minor reaction pathways, were not the focus of this study. Such efforts are valuable, but are feasible only when smaller numbers of HAPs are addressed (e.g., 3).

## RESULTS AND DISCUSSION

The results of this survey are compiled in a 34-page table, with an associated list of over 140 citations to relevant literature (4). The data table lists all 189 chemicals in the same order as in the CAAA, and includes the name and CAS number for each compound, the chemical formula/structure, the major removal processes, the atmospheric lifetime, the potential transformation products, the references for the data presented, and any additional comments. Of the 189 HAP compounds, 92 (49% of the list) have data entries that include reaction rates and corresponding atmospheric lifetimes, as well as identified reaction products. Included in these 92 compounds are 13 chemicals not expected to undergo significant transformation. For eighty-five other compounds (45%) reaction process and lifetime data were found, but no identified reaction products. The remaining 12 compounds were not reported in the literature reviewed; i.e., no information at all was found on their atmospheric reactivity.

A breakdown of the data obtained during this survey, summarized by the chemical classes used in the search, is shown in Table 1. This table shows that there were 97 compounds for which no product information was found (85 no product data + 12 no data at all). The nitrogenated organics and oxygenated organic compounds comprise nearly two-thirds of the group for which no products were identified. This may reflect the lack of definitive methods for measuring these polar VOCs and consequently the absence of data associated with the degradation of these compounds. Methods development for polar VOCs may be necessary before transformation products can be identified.

The major removal process driving the transformation of the HAP compounds in the atmosphere is the reaction with hydroxyl radicals, OH. Of the 177 HAPs for which reaction processes are reported, 146 are primarily attributed to OH. Reactions with ozone, nitrate radicals, liquid and vapor phase water, and by photolysis are generally secondary to OH oxidation, but account for the major removal process for 16 of the

HAPs. For 15 compounds, deposition was identified as the major removal process. Fourteen of these latter HAPs are classified as inorganics and are not expected to undergo rapid chemical transformation in the atmosphere. Physical processes thus dominate their removal from the atmosphere.

The atmospheric lifetimes of the HAP compounds are shown in Table 2. For 177 of the chemicals lifetimes are reported. The table indicates that 81 of the compounds are expected to be transformed in < 1 day. Such rapid removal generally reflects rapid oxidation with OH. A total of 34 compounds fall into the category of being transformed within a 5-day residence time in the atmosphere. In general, these compounds also undergo OH reaction, only at a slower rate. Five HAP compounds are reported as persisting for a range of 1 to >5 days. OH is again indicated as the primary removal process. Finally, 57 chemicals are expected to persist for > 5 days. These compounds either react very slowly or are not expected to be transformed at all and therefore are removed by physical deposition. A review of the lifetime data indicates that hydrocarbons, nitrogenated organics, aromatic compounds, phthalates, sulfates, and pesticides/herbicides are generally expected to degrade rapidly in the atmosphere. The oxygenated organics range evenly across the reported lifetime ranges. The inorganics, halogenated hydrocarbons, and halogenated aromatics are anticipated to be relatively persistent in the atmosphere.

The reaction products reported for the HAPs reflect a wide range of chemical compositions. In general, the HAP compounds undergo atmospheric reactions to generate low molecular weight aldehydes, alcohols, organic acids, ketones, nitrates, carbon monoxide, carbon dioxide, and water. Atmospheric reactions of many of the HAPs generate other HAP species. Production of formaldehyde in the photochemical oxidation of many volatile compounds is a good example of this. Other HAP transformations also produce a variety of stable organic and inorganic compounds that are considered toxic and therefore contribute to public health risks, but which are not designated as HAPs. For 97 of the HAPs, no product data were identified. Continued efforts should be made to identify atmospheric reaction mechanisms and products for these chemicals.

It is important to note that some non-HAP compounds undergo atmospheric transformations to generate hazardous chemicals. An example is propylene. This common ambient air constituent when irradiated in the presence of NO<sub>x</sub> degrades to formaldehyde, acetaldehyde, peroxyacetyl nitrate, nitric acid, propylene glycol dinitrate, 2-hydroxy propyl nitrate, 2-nitropropyl alcohol, α-nitroacetone, and carbon monoxide (5). Other as-yet unidentified mutagens are also formed, and likely include organic peroxides and nitrates. Further investigations of the transformation of propylene with O<sub>3</sub> (6) and by hydroxyl and nitrate radical reactions (7) also identify organic oxygenates being generated although they do not account for the key mutagens associated with NO<sub>x</sub> transformation. This work shows that non-HAP compounds, present in ambient air and considered non-toxic, can go through atmospheric transformations to generate toxic chemicals. This potential source of toxic chemicals in the atmosphere beyond the HAPs list deserves further consideration.

## CONCLUSIONS AND RECOMMENDATIONS

The conclusions of this study are:

- (1) Reaction with OH radical is the most common atmospheric reaction pathway for the HAPs.
- (2) The most common products generated during atmospheric reaction of the HAPs include low molecular weight aldehydes, alcohols, organic acids, ketones, nitrates, carbon monoxide, carbon dioxide, and water. Several of these and other transformation products are considered toxic and may pose a human health risk.
- (3) Atmospheric reaction products are unknown for 97 of the 189 HAPs compounds, and further research needs to be carried out on these chemicals.

The recommendations from this study are:

- (1) Analytical methods development followed by atmospheric transformation studies for those HAPs for which data appear to be lacking.
- (2) Identification of reaction products of non-toxic ambient air constituents to define the human health risk associated with the atmospheric degradation of these non-HAP compounds.

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TABLE 1. DATA COMPLETENESS BY COMPOUND CLASS

Compound Class	Complete Data	No Product Data	No Transformation Anticipated	No Data
Hydrocarbons	3	0	0	0
Halogenated Hydrocarbons	18	8	1	1
Aromatic Compounds	14	3	0	1
Halogenated Aromatics	4	4	0	0
Nitrogenated Organics	10	33	0	6
Oxygenated Organics	18	21	0	1
Pesticides/Herbicides	4	10	0	1
Inorganics	19	2	12	2
Phthalates	0	4	0	0
Sulfates	2	0	0	0
<b>TOTAL</b>	<b>92*</b>	<b>85</b>	<b>13</b>	<b>12</b>

(\*) Includes the 13 compounds that are not anticipated to undergo any atmospheric transformations.

TABLE 2. ATMOSPHERIC LIFETIMES OF HAP COMPOUNDS  
(in days)

Compound Class	<1	<1 to 1-5	1-5	1-5 to >5	>5	No Estimate	Totals
Hydrocarbons	2	0	1	0	0	0	3
Halogenated Hydrocarbons	5	2	1	0	18	1	27
Aromatic Compounds	12	2	2	0	1	1	18
Halogenated Aromatics	0	0	1	1	6	0	8
Nitrogenated Compounds	32	1	2	3	5	6	49
Oxygenated Compounds	10	3	15	0	11	1	40
Pesticides/Herbicides	13	0	0	0	1	1	15
Inorganics	3	0	3	1	14	2	23
Phthalates	2	0	1	0	1	0	4
Sulfates	2	0	0	0	0	0	2
<b>TOTAL</b>	<b>81</b>	<b>8</b>	<b>26</b>	<b>5</b>	<b>57</b>	<b>12</b>	<b>189</b>

*Session 5*

*Integrated Air Cancer Project*

## **The Integrated Air Cancer Project: Overview of Roanoke Study and Comparison to Boise Study**

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### **INTRODUCTION**

The Integrated Air Cancer Project (IACP) is a long-term EPA research project designed to improve understanding of the human exposure to and origins of carcinogenic pollutants. The IACP has focused on products of incomplete combustion (PICs). The goals of the research program are (1) to identify the principal carcinogens in the air to which humans are exposed, (2) to determine which emission sources are the major contributors to the atmospheric burden of carcinogens, and (3) to improve the scientific capability for estimating both human exposure and the resultant comparative human cancer risk arising from exposure to air pollution, particularly those from the PICs. Incomplete combustion products include polycyclic organic matter (POM) primarily adsorbed to respirable particles. PICs were identified as a major source of carcinogenic risk in urban areas and constitute a large fraction of the atmospheric burden of pollutants on a national basis<sup>1,2</sup>. Therefore, the research strategy focused on PICs, especially those from residential home heating and motor vehicles that are major, ubiquitous emission sources in populated areas<sup>3</sup>.

Two residential heating sources have been studied, residential wood combustion (RWC) and residential distillate oil combustion (RDOC). RWC source was selected because: (1) it represented a major fraction of PIC emissions on a national basis; (2) it was under review for regulatory action; and (3) the high mass loadings associated with wood smoke would ensure that sufficient mass could be collected during the field study to, in turn, conduct the chemical and biological analyses needed to progress toward the IACP goals. The first major field study was conducted in Boise, ID, in 1986-1987 where the airshed contained two major sources, mobile source emissions and RWC<sup>4</sup>. The second study, in Roanoke, VA, in 1988-1989 (October to February) was in an airshed containing three sources, mobile sources, RDOC, and RWC<sup>5</sup>.

### **SELECTION AND DESCRIPTION OF STUDY SITES: ROANOKE AND BOISE**

Boise and Roanoke were each selected from a relatively large list of towns and cities initially developed through EPA's National Emissions Data System (NEDS) data base combined with information on concentrations of particulate matter found in these cities. Cities with complex industrial sources, unrepresentative meteorological conditions, and low pollution levels were eliminated. In the selection of a city where RDOC

was a major contributor to the home heating, the cities were ranked by the quantity of oil burned per person and per square mile of urban area. A similar ranking was done in the case of RWC. The top 3-5 locations were site visited by an EPA team and the final city chosen based on the site selection criteria established for each study. These criteria included: (1) The residential heating sources being studied (wood combustion in Boise and oil combustion in Roanoke) were estimated or known to be significant contributors to high particle loadings which normally occurred during the fall and winter; (2) the airshed was determined to be relatively simple, with no major confounding emission sources; (3) there were numerous sampling sites available in the area which met the criteria for the objectives of this study; (4) the terrain and meteorology was appropriate for extrapolation to other locations; and (5) the support of local and State government as well as local civic and business leaders.

These field studies in Boise and Roanoke were conducted in metropolitan urban areas with populations between 100,000 and 150,000. Both cities are governmental, educational and commercial centers for their region. Geographically they are both located in valleys adjacent to or between large mountain ranges. This local topography and the meteorological conditions for both sites resulted in periods of winter inversions. There are no large or heavy industrial sources in either city. A detailed description comparing these two sites and average pollutant concentrations is reported elsewhere<sup>5,6</sup>. Important differences between these two locations and studies include: (1) the Boise airshed contained only mobile source emissions and RWC while the Roanoke airshed contained a third source, RDOC, and (2) the background pollution levels coming into the Boise airshed from the surrounding region were much lower than for Roanoke where the background sulfate concentrations were twice the levels of Boise presumably due to the influence of industrial emissions on the Eastern US corridor.

## **SURVEY AND INVENTORY OF POLLUTION SOURCES AND PERSONAL ACTIVITY PROFILES**

Surveys were used to learn more about the major sources of PICs in each of these airsheds. Two surveys were used, the first was a general survey dealing with home heating and motor vehicle usage. A second survey was administered to respondents who burned wood (in Boise and Roanoke) and oil (Roanoke only) to determine the type of heating appliance, usage, etc. In addition to these surveys, a micro-inventory of each city's potential pollution sources was conducted<sup>7,8</sup>.

A survey of home heating sources and motor vehicle usage in Roanoke<sup>9</sup> and Boise<sup>10</sup> was administered using a probabilistically-derived sample of the housing units based on block-census data for the cities of Boise and Roanoke. Figure 1 compares the residential heating sources for these two cities during the IACP field studies. Roanoke has a substantially lower percentage of the residences using wood as a heating source (10%) compared to Boise (62%). Roanoke has an additional source of residential distillate oil heating (22% of the residences).

One of the goals of the IACP is to improve EPA's ability to assess exposure and risk from airborne carcinogens. To address this issue, the IACP included efforts to characterize both outdoor and indoor exposure levels and to improve our understanding of the relationships between indoor and outdoor concentrations of carcinogens. The residential sampling portion of the field studies are critical to the exposure estimate, because people normally spend about two-thirds of their time in their houses. The indoor sampling provides insight and data that can be used to estimate indoor exposures by the population in Boise. In addition, residents completed daily "diaries" of their activities during sampling studies at their homes. Diaries were compiled in Boise and in Roanoke to estimate the fraction of time spent in different locations or activities.

The daily activity diaries from the Boise and Roanoke studies were used to characterize the average time periods spent in five microenvironments: indoors at houses (67-69%); outdoors (1-2%); in-transit (3-4%); at the work place (16-18%); and at other indoor locations like stores, churches, and post offices (8-12%). The percentage of time spent in each of the five zones for these winter periods was determined from the diaries and compared to a national survey<sup>11</sup> for year-round activity patterns. The time allocations for both Boise and Roanoke were reasonable compared with the national survey data. One would expect the time indoors during the winter to be greater than the national annual average, and for the time outdoors to be less. Boise and Roanoke are modest sized cities, so the commute time, T, would also be expected to be less than the national average. These expected differences from the national average were observed, however the differences were minor (max 4% variation).

The relatively uniform distribution of pollutants across these two airsheds and across the population distribution facilitates the exposure extrapolation for many of the PIC pollutants from the relatively small population for which we obtained time-activity profiles to the general populations in these airsheds. In the Boise study, human exposure and dose estimates have been completed for the extractable organic mass (EOM) from fine particles and the exposure apportioned between the two major sources in the airshed<sup>11,12</sup> using methods developed as part of the IACP<sup>11,13</sup>.

## **FIELD STUDY DESIGN**

The field studies were conducted in the winter months, over a four month period, during the heating season in Boise, ID in 1986-87, and in Roanoke, VA in 1988-89. The field program consisted of both ambient and residential sampling. The data generated in the sampling programs have been detailed in several papers on Boise<sup>14</sup> and Roanoke<sup>5,6</sup>.

The ambient sampling was conducted at three primary sites and four auxiliary sites in each city as shown in Figures 2 and 3. One primary site in each city was in a residential area. A second primary site was near well-traveled roadways. A third primary site was the background sampling location. Four auxiliary sites were also operated during these studies. Sampling periods were 12 hours long, with changeover times at 7 A.M. and 7 P.M. There were 13 sampling periods scheduled per week, and one period was dedicated to calibration, maintenance, etc.

The residential sampling involved a matched pair of nearby houses each week. During the study, ten pairs of houses were sampled. One of the houses in each pair used a combustion heating device (RWC in Boise and RDOC in Roanoke). The other house was heated by electricity or natural gas and did not use either RWC or RDOC. Sampling was conducted in 12 hour periods identical to those at the ambient sampling sites. Sampling began each Saturday morning and terminated after the nighttime sampling period, which ended at 7 A.M. Wednesday. For analysis purposes, the eight sampling periods were combined into four samples: weekend daytime, weekend nighttime, weekday daytime, and weekday nighttime. Whenever samples were collected at the houses, corresponding samples were also taken at the primary sites. Samples of the RWC emissions from the wood burning appliances in Boise<sup>15</sup> and residential oil heaters in Roanoke<sup>16</sup> were obtained with a dilution sampling system<sup>17,18</sup>. Each pair of houses was matched for age, size, etc. None of the residents in the sampled houses were smokers.

The maps of Boise (Figure 2) and Roanoke (Figure 3) show the primary, auxiliary, and residential sampling locations. Each R number on the map represents a matched pair of houses. The auxiliary sites were located across the valley in order to examine the distribution of pollutants across the airshed. Resource limitations prevented the design of a residential monitoring study sufficiently large to represent the populations statistically. Although the 10 pairs of houses were not statistically representative of the Boise population, the data may be used to understand the processes that affect exposures across the community. In addition, the auxiliary sites provided supplementary data to support the extension of population exposure assessment across the total population.

### **CENTRALIZED DATABASE**

Data from the sampling, chemical analysis, physical analysis and biological studies have been integrated into a centralized database. All of the data have been validated by the EPA scientist or engineer responsible for those measurements. The database is implemented in a fourth generation, non-procedural, report generation system (FOCUS®) on the National Computing Center IBM 3090, at Research Triangle Park, NC. The database for Boise contains approximately 185 unique analysis species and more than 78,400 data values and the database for Roanoke will be somewhat larger. The database is described in detail elsewhere<sup>4</sup> and is now available from EPA<sup>4</sup> in a format suitable for personal computer use (dBase®).

### **COMPARATIVE CARCINOGENICITY AND SOURCES OF CANCER RISK**

The component of PICs estimated to make the largest contribution to human cancer risk is the polycyclic organic matter (POM) associated with airborne particles. The extractable organic matter (EOM) adsorbed to airborne particles contains most of the carcinogenic POM. Under some ambient conditions, the semivolatile organic compounds (SVOCs) may also contain polycyclic aromatic compounds. The carcinogenicity of SVOCs has not yet been studied. The Boise IACP project, for the first time, both source apportions<sup>19</sup> and characterizes the carcinogenicity of ambient POM from particles using in vivo animal tumor assay<sup>19</sup>, receptor modeling<sup>20,21</sup> and human

exposure data<sup>12</sup>. In Boise, the ambient POM sample containing 33% contribution of motor vehicle emissions was more than twice as tumorigenic as the ambient sample with only 11% motor vehicle emissions. Receptor modeling of the EOM in Roanoke is reported in this volume<sup>22</sup> and the animal tumor studies are in progress. Atmospheric transformations in these airsheds<sup>23</sup> are contributing to the presence of air toxics and may account for a component of the increased tumorigenicity associated with the POM from mobile sources<sup>4</sup>. Nitrogen oxides appear critical in the formation of mutagenic transformation products.

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## Residential Heating Sources

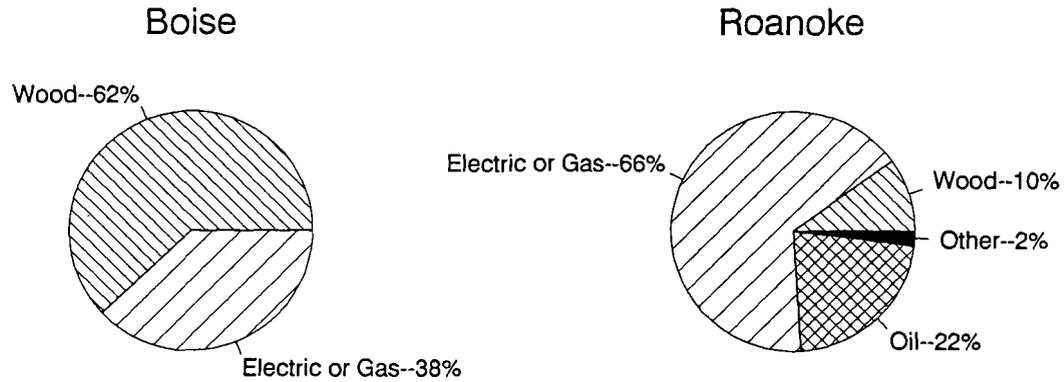


Figure 1. Survey of residential heating sources.

**IACP  
Sampling Sites  
1986 - 1987  
Boise, Idaho**

- (P)** Primary Sites  
EGP  
FS  
RCAG
- (A)** Auxiliary Sites  
FAIR  
CBP  
WINS  
ADAM
- ▲** Residential Sites

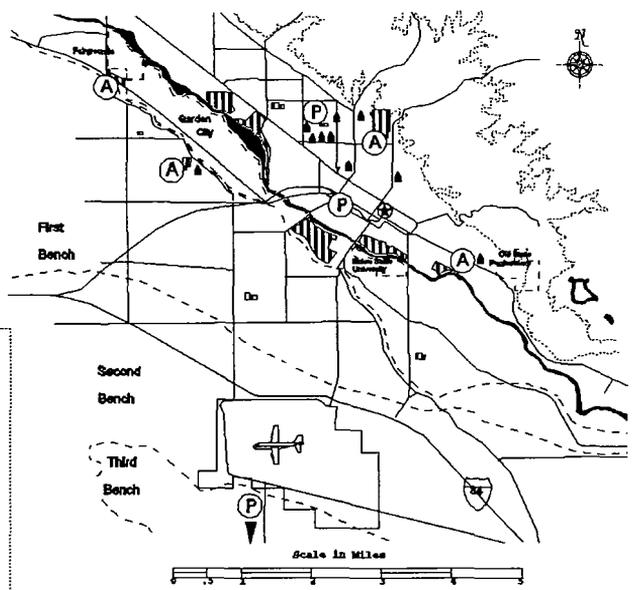


Figure 2. Map of Boise, ID, Showing Sampling Sites

IACP ●  
Sampling Sites  
1988 - 1989  
Roanoke, Virginia

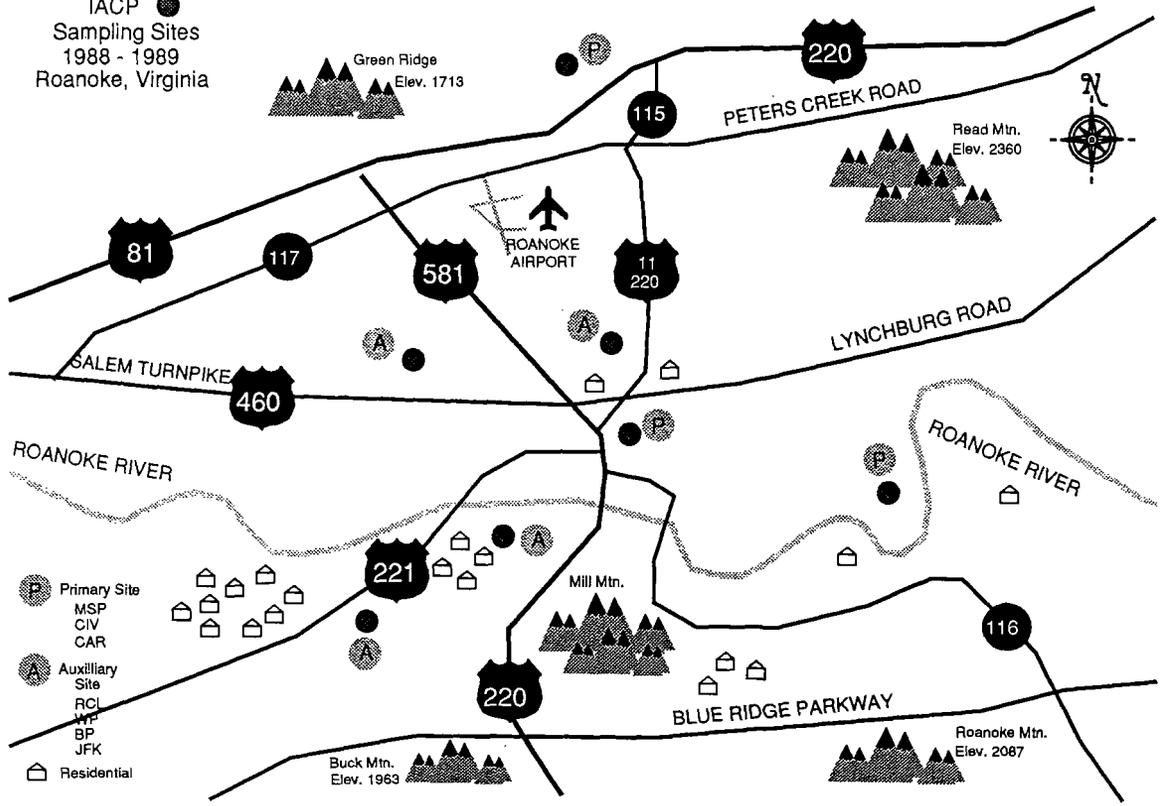


Figure 3. Map of Roanoke, Virginia showing sampling sites.

## **A Comparison of Air Quality Measurements in Roanoke, VA, and Other Integrated Air Cancer Project Monitoring Locations**

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### **ABSTRACT**

As part of the U.S. Environmental Protection Agency's Integrated Air Cancer Project (IACP) field air quality monitoring studies in four U.S. cities were conducted between 1984 and 1989. The chronology of the field studies was: December 1984 to March 1985 in Albuquerque, NM; (2) January 1985 to March 1985 in Raleigh, NC; (3) December 1986 to March 1987 in Boise ID; (4) October 1988 to February 1989 in Roanoke, VA. Aerosol and gas phase pollutants collected at these locations were used in receptor models to apportion the contributions of emissions from wood burning and mobile sources to fine particle organic matter concentrations. This paper compares the composition of air pollutants measured in the four IACP studies, with regard to temporal variation and geographic location.

### **INTRODUCTION**

Between 1984 and 1990, the U.S. Environmental Protection Agency (U.S. EPA) conducted a series of field investigations to collect air quality and source emission samples for subsequent chemical characterizations. These studies were part of the U.S. EPA's Integrated Air Cancer Project (IACP), whose objectives were to identify the principal airborne carcinogens, determine which emission sources were the major contributors of carcinogens to ambient air, and to improve the estimate of human exposure and comparative human cancer risk from specific air pollution emission sources.<sup>1</sup> Unlike past efforts to identify airborne carcinogens through the use of emission inventories, the IACP took the approach of measuring the mutagenicity (a surrogate for carcinogenicity) directly and apportioning this property to source types.<sup>2,3</sup>

Field air quality monitoring studies in four U.S. cities were conducted between 1984 and 1989. The following is the chronology of these field studies: (1) December 1984 to March 1985 in Albuquerque, NM, (2) January 1985 to March 1985 in Raleigh, NC, (3) December 1986 to March 1987 in Boise, ID, and (4) October 1988 to February 1989 in Roanoke, VA.<sup>3,4</sup> In the studies performed in Raleigh and Albuquerque, measurements were made of the concentrations of selected elemental tracers associated with emissions from wood stoves and motor vehicles. Potassium (K) corrected for soil content<sup>2,3</sup> was measured as a species emitted during the combustion of wood, and lead (Pb) and bromine (Br) were determined because they are elements emitted from motor vehicles using leaded gasoline. In the studies conducted in Boise and Roanoke, volatile organic compounds (VOCs) characteristic of mobile source emissions<sup>5</sup> were found to be a replacement for Pb and Br as receptor modeling tracers.

This current work compares results of air quality measurements made in four cities where samples were collected and analyzed to provide the data to support the IACP study objectives.

### **EXPERIMENTAL**

Overviews of the sample collection and analysis for IACP studies have been given in previous publications.<sup>3,4</sup> The basic collection and analysis methods used to develop the data base to support the receptor modeling for the four IACP studies are given in Table 1.

In these IACP field studies, air quality data and samples were collected at three primary sites. One site was at a background location (except in Albuquerque), and two sites were in urban locations. In each city, one primary site was a residential location impacted by wood smoke emissions, and the second primary site was located near a major roadway impacted by motor vehicle emissions. Aerosol and VOC samples were collected at these primary sampling locations at 12-h intervals beginning at 7 a.m. and 7 p.m. in order to represent daytime and nighttime conditions. A complete description of the monitoring performed at these sites has been described elsewhere.<sup>1-4</sup>

In the Roanoke study, nonradioactive organometallic rare earths (<sup>152</sup>Sm and <sup>149</sup>Sm) were added to the residential home heating oil supplies and to diesel fuel used by the local buses as possible tracers for these sources.<sup>6</sup> Samples collected at the residential and roadway primary sites were analyzed for <sup>149</sup>Sm and <sup>152</sup>Sm content.

## RESULTS AND DISCUSSION

Table 2 contains the average composition of the fine particles collected in the four IACP cities. There are several important features of the fine particles, characteristic of these cities, that are related to the time and location of the studies. For example, in Albuquerque, the soil-corrected K concentration is substantially lower than that in the other three cities. This observation is primarily related to the lower K content of the wood fuel (Pinon pine) typically used in this city.

The Pb concentration in the fine particles decreased from a high of 237 ng/m<sup>3</sup> in Albuquerque in 1985 to 26.9 ng/m<sup>3</sup> in Roanoke in 1989. This coincides with the reduction of Pb in gasoline over the past 20 years mandated by Federal law.

The sulfur content of the fine particles in Raleigh and Roanoke was substantially higher than that in the western cities. This difference is likely to be in part related to the higher density of power plant activities that use coal and diesel fuel (which contains sulfur) in the eastern United States as compared to the lower density in Boise and Albuquerque.

Table 3 contains a comparison of the key receptor modeling species measured at the four study locations. The variations in the Pb and K values mentioned above are clearly shown in Table 3. In addition, the carbon (volatile carbon [C<sub>v</sub>], elemental carbon [C<sub>e</sub>], and extractable organic matter [EOM]) content of the fine particles in Roanoke were substantially lower than the values measured in the other cities. Correspondingly, the mutagenicity of the EOM samples from Roanoke was also one half the value or more of the mutagenicity measured at the other IACP locations (Table 2).

In Roanoke, the average fine particle concentration and average coarse particle concentration measured at the main monitoring site, which was at the convention center near Interstate 581, were 26.3 and 14.4 µg/m<sup>3</sup>, respectively. This was 35% higher than the average value for the main monitoring site located at Morningside Park (residential location) and twice the concentration measured at the background location at Carvin Grove Reservoir. The elevated concentration levels at the convention center location are for the most part related to the high density of motor vehicles passing the site on Interstate 581 and the close proximity (5m) of the site from the highway.

In Roanoke and Boise, values for the nighttime fine particle mass and extractable organic mass at the urban primary sites were typically 40% larger than daytime concentrations. For example, in Boise at the residential primary site, the nighttime fine particle mass averaged 47 µg/m<sup>3</sup>, whereas the daytime values were 28 µg/m<sup>3</sup>. These differences were associated with the increased use of wood stoves for heating at night and, in some cases, nighttime meteorological inversions.

A number of the VOCs measured in Boise and Roanoke were highly correlated with the Pb concentrations in fine particles.<sup>3</sup> This relationship has led to utilization of VOCs as a replacement for Pb as a receptor modeling tracer for fine particle emissions from motor vehicles.<sup>7</sup> Table 4 contains the average a.m. and p.m. concentration of selected VOCs and total nonmethane hydrocarbons (NMHC) measured in Boise and Roanoke. The VOCs with elevated concentrations shown in Table 4 were species that correlated with elevated fine-particle Pb concentrations.<sup>5</sup> This relationship provided the impetus to test VOCs as candidates to replace Pb as a tracer for fine particle emissions from motor vehicles.<sup>7</sup> This research also has led to the development of chemical mass balance models for VOCs that have the potential to be used to validate VOC emission inventories.<sup>8</sup>

## SUMMARY

The following is a summary of the results obtained from the IACP monitoring studies in the four cities where air quality samples were collected. The observations discussed in this summary are derived from limited, measurements collected during wintertime periods at selected locations in these four cities, therefore, extrapolation of the data in this report to assess overall air quality in these cities beyond the period of the studies is not recommended.

1. Fine particle sulfate concentrations in Raleigh, NC, and Roanoke, VA, were twice the levels of those in Boise, ID, and Albuquerque, NM.
2. Lead concentrations dropped from 237 ng/m<sup>3</sup> in Albuquerque in 1985 to 27 ng/m<sup>3</sup> in Roanoke in 1989.
3. The fine particle K (soil corrected) in Albuquerque was one third the level in Raleigh, Boise, and Roanoke.
4. Total NMHC in the four cities was approximately the same, 500 ppbC.
5. Extractable organic matter in Roanoke was one half the levels of the other three cities.
6. Nighttime EOM concentrations in all cities were higher than daytime values.
7. In Boise and Roanoke, the mass of fine particulate fraction was 2 to 3 times higher than the coarse fraction, as measured by the dichotomous sampler.
8. In Boise and Roanoke, VOCs at the roadway and residential sites were dominated by aliphatic hydrocarbons, which are composed of species related to mobile source emissions.

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## DISCLAIMER

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Table 1. Collection and analysis methods for four IACP studies.

Sampler Type	Sampling Medium	Site Category	Analysis
PM10 Dichotomous	Teflon	primary auxiliary residential	mass XRF
PM2.5 Hi-Vol	TIGF	primary, aux.	mutagenicity
PM10 Medium Vol	Quartz	primary	<sup>14</sup> C and rare earths
	Quartz	primary	C <sub>6</sub> , C <sub>v</sub>
	XAD	residential	SVOCs
VOC/Aldehyde	DNPH tubes	primary	aldehydes
	Canisters	residential	VOCs
Annular Denuder	Filters, tubes	primary	acidic gases
Continuous Parameters		primary	
CO, NO <sub>x</sub> , O <sub>3</sub>		residential	
Meteorological Parameters		primary	
ws, wd, t, RH, SR		auxiliary	

Table 2. Air quality aerosol data measurements at primary residential sites: Average composition of fine particles.

	Albuquerque (1985-1986)	Raleigh (1985-1986)	Boise (1986-1987)	Roanoke (1988-1989)
Mass	20.6	30.3	35.7	19.9
Al	76.5	9.4	102.3	175.6
As	(0.7)	1.2	1.5	1.8
Br	84.7	27.5	14.4	5.4
Ca	59.0	17.8	25.8	47.2
Cl	36.0	6.9	122.2	52.5
Cr	(1.8)	0.4	0.6	1.1
Cu	(1.5)	19.8	11.3	7.1
Fe	44.5	44.4	22.1	113.6
K	74.2	158.9	144.9	176.8
Mn	(1.0)	2.7	1.7	12.0
Mo	0.2	1.0	1.5	1.3
Pb	237.4	95.6	45.3	26.9
S	507.1	1729.3	602.7	1177.0
Se	0.0	1.5	0.8	1.8
Si	76.0	75.8	69.1	76.6
V	(6.9)	2.5	1.3	4.0
Zn	6.6	15.1	18.5	82.8
K*	54.1	140.3	128.9	151.9
C <sub>6</sub>	2.1	0.5	1.7	1.5
C <sub>v</sub>	13.2	10.0	12.7	7.3
EOM	24.5	20.1	22.0	11.0
Mutagenicity	40.2	20.1	45.8	19.0

\* Mass, C<sub>6</sub>, C<sub>v</sub>, and EOM in micrograms per cubic meter; elements in nanograms per cubic meter; mutagenicity in revertants per cubic meter.

**Table 3. Comparison of average 24-h (7 a.m.-7 a.m.) concentrations of key receptor modeling species at the four cities studied by IACP (data from primary residential site locations).**

Species	Albuquerque (1984-1985)	Raleigh (1984-1985)	Boise (1986-1987)	Roanoke (1988-1989)
Mass $\mu\text{g}/\text{m}^3$	20.6	30.3	35.7	19.9
a.m.	10.7		27.8	17.5
p.m.	29.7		42.2	22.0
Pb $\text{ng}/\text{m}^3$	237.4	95.6	45.3	26.9
a.m.	195.1	82.0	46.9	24.3
p.m.	276.3	117.0	43.4	29.2
K $\text{ng}/\text{m}^3$ *	54.1	140.3	128.9	151.9
a.m.	12.6	72.0	91.5	125.3
p.m.	92.5	175.0	162.0	175.2
Cv $\mu\text{g}/\text{m}^3$	13.2	10.0	12.7	7.3
a.m.			9.4	5.8
p.m.			16.0	8.5
Ce $\mu\text{g}/\text{m}^3$	2.1	0.5	1.7	1.5
a.m.			1.8	1.5
p.m.			1.6	1.5
EOM $\mu\text{g}/\text{m}^3$	24.5	20.1	22.0	11.0
a.m.			16.2	7.0
p.m.			28.1	14.9

\*K corrected for soil content

**Table 4. Comparison of selected VOC values (ppbC).**

Species	Site*	Average	Boise		Average	Roanoke	
			a.m.	p.m.		a.m.	p.m.
Acetylene	Residential	13.2	15.6	10.8	13.4	11.8	15.1
	Roadway	19.3	20.9	17.6	25.5	21.0	29.9
Benzene	Residential	13.5	13.0	14.0	7.4	6.1	8.8
	Roadway	18.4	18.8	18.0	12.9	10.0	15.6
2-Methylpentane	Residential	9.8	9.8	9.9	6.2	3.0	4.5
	Roadway	16.0	17.0	14.9	11.1	6.2	8.7
2-Methylhexane	Residential	8.4	8.3	8.4	3.6	2.7	4.4
	Roadway	13.8	14.6	12.9	6.8	5.0	8.7
Toluene	Residential	25.5	25.3	25.6	15.5	12.9	18.3
	Roadway	42.1	44.0	40.0	30.4	23.9	36.8
Total Nonmethane Hydrocarbons	Residential	455.6	453.2	458.0	334.3	280.0	390.0
	Roadway	636.4	656.7	615.5	624.4	438.0	806.0

\* Primary sites.

## **Mutagenicity of Indoor and Outdoor Air in Boise, Idaho and Roanoke, Virginia**

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### **ABSTRACT**

The mutagenicity of ambient air samples, collected in two large field studies was examined using the Salmonella microsuspension bioassay.<sup>1,2</sup> The first study was conducted during the 1986-1987 winter heating season in Boise, Idaho. The second study was conducted in Roanoke, Virginia from October 1988 to February 1989. The study design for both sampling locations was very similar and has been described previously.<sup>2</sup> The field studies consisted of an ambient air component at stationary primary site locations and a residential component that involved sampling different homes each week. The primary sites included a location dominated by residential heating emissions, a site dominated by mobile source emissions, and a background site. The residential study component consisted of twenty homes being sampled in matched pairs (10 pairs) over a four-day weekend and weekday period. Each pair of homes included one home which operated either a residential oil heater or wood burning appliance (e.g. wood stove or fireplace) and the other home did not. The Salmonella mutagenicity (revertants/m<sup>3</sup>) of both particle samples (collected with PM10 medium flow (0.113 m<sup>3</sup>/min) samplers) and semivolatile organic compound (SVOC) samples (collected on XAD-2 cartridges) was determined by simultaneous collection of indoor and outdoor samples from each pair of homes. The initial results of these studies have shown that outdoor air significantly influences the mutagenicity of particles indoors. The concentration of particle mutagenicity indoors is consistently lower than outdoors by a factor related to the particle infiltration rate. The concentration of mutagenicity from the SVOCs indoors is greater than outdoors and may be related to indoor sources.

### **INTRODUCTION**

Ambient aerosols (particle matter) in urban areas typically contains condensed organic matter from combustion emissions. A number of studies have shown that the extractable organic matter (EOM) from air particles is carcinogenic in animals and mutagenic in short term bioassays<sup>4</sup>. Short term mutagenicity bioassays have been used in ambient air monitoring studies and chemical characterization studies in order to identify the major emission sources and compounds which contribute to the mutagenic activity of air particulate extracts<sup>5,6</sup>. Small area combustion sources, primarily vehicles and home heating sources, have been shown to account for most of the mutagenic activity associated with air particulate matter in several urban areas<sup>6,7</sup>. These studies were designed to estimate the

contribution of combustion sources to the cancer risk in ambient urban aerosol in a relatively simple airshed.

The US EPA's Integrated Air Cancer Project (IACP) is a multi-year research program which set as one of its primary goals identification of the major sources of cancer risk in urban air<sup>8,9</sup>. The first study in Boise focused on a relatively simple airshed containing two major area sources (wood burning and motor vehicles) and no major industrial sources. The second study in Roanoke continued the same design with the addition of residential oil burning. This paper describes the microsuspension mutagenicity studies conducted on aerosol samples collected in Boise and Roanoke.

## **EXPERIMENTAL METHODS**

### Experimental Design

The overall IACP program<sup>8,9</sup> and field study design<sup>10</sup> and sampling methodologies<sup>11</sup> have been previously reported. Two primary sites were selected to represent a residential wood smoke impacted area with minimal mobile source impact [Elm Grove Park (EGP) Site in Boise and Morning Side Park (MSP) in Roanoke] and a site with maximal mobile source impact [Fire Station (FS) Site in Boise and the Civic Center (CIV) in Roanoke], located near a major intersection where the mobile sources included a mixture of heavy duty and light duty diesel and gasoline vehicles.

The residential sampling involved pairs of homes. Each pair of homes included one home which operated a wood burning appliance (e.g. wood stove or fireplace) or oil burning furnace and the other home did not. None of the homes used in this study had other unvented stoves (e.g. kerosene heaters) or tobacco smoking residents. The homes were matched as closely as possible with respect to age, size and other factors and were located as closely as possible to each other and the ambient monitoring sites.<sup>3,12</sup>

The pair of homes were sampled simultaneously. A total of 20 homes, in each study, were sampled and the homes without the wood or oil burning appliances were also sampled outside the home. This design allowed a comparison of homes with and homes without wood burning or oil burning and also comparison of inside and outside the homes. Sampling started at 7:00 am Saturday and samples were collected every 12 hours until Wednesday at 7:00 am. A total of eight 12-hour samples were collected on two weekend days and two weekdays at each home. Sampling at the primary sites followed this same schedule.

Samples for bioassay were collected using PM10 medium flow (0.113 m<sup>3</sup>/min) samplers with a size selective inlet to exclude particles greater than 10 μm. The particles less than 10 μm were collected on Pallflex 102 mm T60A20 Teflon-impregnated glass fiber filters. Semivolatile organic compounds were collected on XAD-2 canisters which were placed after the filter. The complete description of the entire residential sampling and analysis is reported elsewhere.<sup>12</sup>

All filter samples for the bioassay studies were transported on dry-ice and stored at

-80°C from the time of collection until extraction. The filters were combined in Soxhlet devices and extracted for 24 hours with dichloromethane and the extracts filtered (0.2µm Millipore-type FG filters). The extracts were concentrated on a rotary evaporator with a 35°C water bath to reduce the volume prior to quantitative transfer to volumetric flasks. A portion of the extract was used for a gravimetric determination.

### Sample Composites

The amount of extractable organic matter (EOM) needed for mutagenicity testing required the compositing of samples. Weekend daytime (Saturday 7am and Sunday 7am) were composited for one sample, likewise the weekend nighttime samples (Saturday 7pm and Sunday 7pm) were composited for one bioassay sample. The weekday (Monday and Tuesday) samples followed the same design. The composite samples were assigned unique numbers throughout the study. The filter samples containing the particles and the XAD-2 samples containing the semivolatiles were both composited using this design.

### Mutagenicity and EOM Methods

The Ames Salmonella typhimurium microsuspension assay was conducted by previously published guidelines<sup>1,3</sup> in tester strain TA98 both with (+S9) and without (-S9) a metabolic activation system provided by an Aroclor induced CD-1 rat liver homogenate. The dose range used was from 0.1, 0.3, 0.5, 1.0, 3.0, 5.0 and 10.0 cubic meters (m<sup>3</sup>) per plate with 2 plates per dose. Each assay included negative (solvent controls) and the appropriate positive control chemicals for TA98 (+ and -S9) for quality control. The initial linear slope of the dose response curve was analyzed using the method of Bernstein et al<sup>12</sup>. All samples were analyzed in two separate experiments and the data were summarized together.

Gravimetric measurements were also performed on each of these samples to determine µg of extractable organic material (EOM). The mutagenic response is expressed as revertants/m<sup>3</sup> and the µgEOM/m<sup>3</sup> can be calculated.

## **RESULTS AND DISCUSSION**

### Mutagenicity of semivolatile and particle samples

The mutagenicity testing on both the semivolatiles and the particle samples were conducted on a per cubic meter of air sampled. Separate samples were collected at the primary sites during the same sampling times to determine fine particle mass, therefore, percent extractables could be estimated. Table 1 shows the fine particle mass and EOM for the primary sites at Boise and Roanoke in the daytime samples and nighttime samples. The fine particle mass collected at the different sites varies. However, the estimated percent EOM between the daytime and nighttime in Boise varies only a few percent. The daytime percent extractable at EGP is 55% compared to 53% for the nighttime sample. However, the difference in the estimated percent extractables between the daytime and nighttime in Roanoke is greater. The percent extractable at MSP increases from 35% for the daytime sample to 68% for the nighttime. The fine particle mass for MSP increases from 17µg/m<sup>3</sup>

to  $22\mu\text{g}/\text{m}^3$ , a 29% increase but the EOM increases from  $6\mu\text{g}/\text{m}^3$  to  $15\mu\text{g}/\text{m}^3$ , a 150% increase. This difference in the EOM indicates that the composition of the samples is different. The higher percent EOM is likely to be due to an impact from wood smoke emissions that has a much higher % EOM than mobile sources or residential oil burning.

Table 1. Comparisons of Primary Site Day and Night Fine Particle Mass and Particle EOM in Boise and Roanoke (Micrograms per cubic meter).

City	Site	Mass AM	EOM AM	% Ext.	Mass PM	EOM PM	% Ext.
Boise	EGP	27	15	55	43	23	53
	FS	24	11	46	39	20	51
Roanoke	MSP	17	6	35	22	15	68
	CIV	21	8	38	29	20	69

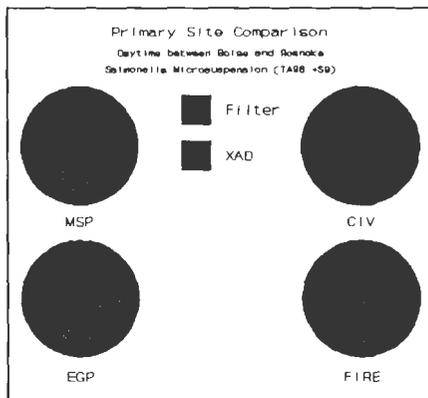
The mutagenicity of both the filter (fine particles) and the XAD-2 (SVOCs) for both cities by both daytime and nighttime are shown in Table 2 in revertants per cubic meter of air. There is little difference in the total mutagenicity between the daytime and nighttime samples in the Boise airshed. However, the mutagenicity increases in the nighttime samples in the Roanoke airshed. This increase in mutagenicity between the daytime and nighttime correlates with the increase in EOM seen in Roanoke.

Table 2. Comparisons of Primary Site Daytime and Nighttime Mutagenicity in Boise and Roanoke. (Revertants per cubic meter)

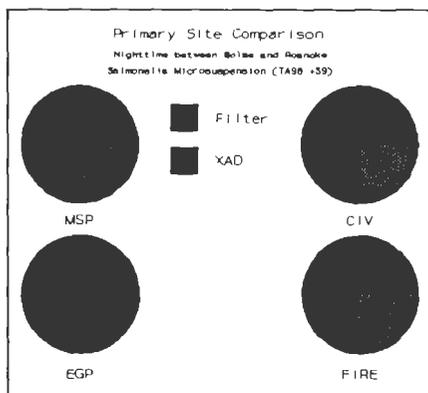
City	Site	Filter AM	XAD AM	Total	Filter PM	XAD PM	Total
Boise	EGP	67	31	98	67	33	100
	FS	73	26	99	67	31	98
Roanoke	MSP	35	19	54	73	30	103
	CIV	56	49	105	119	40	159

The contribution of the semivolatiles (XAD-2) to the total mutagenicity at the primary site for the daytime samples is very similar between the residential primary sites in Boise and Roanoke (EGP and MSP). However, the mutagenic contribution of the semivolatiles from the daytime samples at the Roanoke mobile source primary site (CIV) is greater than that of the Boise mobile source primary site (FS). This is shown graphically in Figure 1.

This difference in semivolatile contribution to the total mutagenicity is not seen in the nighttime samples in Roanoke. The nighttime mutagenicity at the CIV in Roanoke is mostly from the particles on the filter. This suggests that the composition of the airshed in Roanoke varies more from daytime to nighttime than the Boise airshed. The contribution of the filter and XAD to the total has a very similar profile in Boise for both daytime and nighttime. The nighttime comparison of the primary sites is shown in Figure 2. The increase in nighttime total mutagenic potency at MSP would appear to be related to a different species collected on the particles. Whereas the difference in the mutagenic potency of the nighttime sample at the CIV could be related to not only the different species on the filter but also the increase in the mass of the particles collected.



**Figure 1** Daytime Primary Site Comparison between Boise and Roanoke (TA98 +S9)



**Figure 2** Nighttime Primary Site Comparison between Boise and Roanoke (TA98 +S9)

### Indoor and Outdoor Mutagenicity

The residential mutagenicity in both Boise and Roanoke was analyzed to determine indoor and outdoor relationships. Comparisons were made between: homes with wood burning or oil burning (In/With); homes without these heating sources (In/Without); and outside the homes (Out). These samples were composited for the weekend, weekday, daytime, and nighttime sampling periods.

The mutagenic potency as measured in revertants per cubic meter for the homes in Boise and Roanoke is shown in Table 3.

Table 3. Comparisons of Residential Sites Daytime and Nighttime Mutagenicity in Boise and Roanoke (Revertants per Cubic meter)

City	Homes	Filter AM	XAD AM	Total	Filter PM	XAD PM	Total
Boise	Out	61	42	103	61	26	87
	In/ Without	21	16	37	24	21	45
	In/With	28	22	50	27	34	61
Roanoke	Out	40	21	61	54	15	68
	In/ Without	27	13	40	24	15	39
	In/With	15	23	38	27	27	54

\*\*\* In With: Boise homes - heating source wood; Roanoke homes - heating source oil  
 In Without: Boise and Roanoke homes - heating source either natural gas or electric  
 Out: Boise and Roanoke -- outside the homes using either natural gas or electric

The residential outside mutagenicity in Boise was consistent with the EGP mutagenicity measured in both the daytime and nighttime. The Boise daytime mutagenicity was 98 rev/m<sup>3</sup> at EGP (Table 2) and outside the homes the average was 103 rev/m<sup>3</sup> (Table 3). The correlation in Roanoke during the daytime was still similar with MSP at 54 rev/m<sup>3</sup> (Table 2) and outside the homes at 61 rev/m<sup>3</sup> (Table 3). The daytime mutagenicity inside the homes in Roanoke was similar between the homes with and the homes without but was somewhat lower than the outside air. The daytime mutagenicity in Boise was slightly higher in the homes with, in comparison to the homes without but as in Roanoke the outside air was significantly higher. This relationship in Boise could be influenced by one home where the wood stove was known to be leaking and therefore increased the inside emissions.

Correlation analysis of the particle mutagenicity showed the mutagenicity inside the homes was correlated with the mutagenicity of the outside air. When the revertants per cubic meter were plotted for all the homes on the same graph the inside mutagenicity increased and decreased with the outside air. This was observed in both the Boise and Roanoke study.

#### ACKNOWLEDGEMENTS AND DISCLAIMER

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## **Radiocarbon Measurements of Extractable Organic Matter from the Integrated Air Cancer Project Study in Roanoke, VA<sup>1</sup>**

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### **ABSTRACT**

The use of radiocarbon ( $^{14}\text{C}$ ) as a unique discriminator of fossil and modern combustion aerosols has been applied to a number of studies for the purpose of apportioning specific sources of atmospheric pollutants. It has been used previously as part of the measurement program of the U.S. Environmental Protection Agency's Integrated Air Cancer Project (IACP). The objective of the work reported here was to determine the relative contribution of modern and fossil sources on wintertime organic aerosols in wintertime Roanoke, VA (1988 - 1989), as part of the IACP. Radiocarbon measurements were performed on the extractable organic matter (EOM) separated from the fine size fraction of particulate samples collected in Roanoke. Results of these analyses suggest that biogenic carbon, derived primarily from residential wood combustion, was the dominant source of atmospheric aerosol EOM at both the residential and rural background sampling sites. The in town traffic site was more heavily influenced by fossil carbon, derived primarily from motor vehicle emissions.

### **INTRODUCTION**

The use of radiocarbon ( $^{14}\text{C}$ ) as a unique discriminator of fossil and modern combustion aerosols has been applied to atmospheric source apportionment studies of both particles and gases (Klouda, *et al.*, 1986, Sheffield, *et al.*, 1991). In particular, it has been used in several studies conducted as part of the IACP (Klouda, *et al.*, 1987, Klouda, *et al.*, 1991). The objective of the work reported here was to determine the relative contribution of modern and fossil sources to wintertime organic matter extracted from the fine size

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fraction of particulate samples collected in Roanoke during the winter of 1988 - 1989. In all, radiocarbon measurements were made on twenty nine samples and nine filter blank EOM extracts. This paper presents the results of experimental methods, quality control (QC) procedures and  $^{14}\text{C}$  analyses performed in support of this study by us at the National Institute of Standards and Technology (NIST) .

## **SAMPLE HISTORY**

The field sampling and EOM extractions portions of this study were carried out by EPA contract laboratories. These procedures are summarized here.

**Field Sampling:** Fine particulate material, with an aerodynamic diameter of  $<2.5\ \mu\text{m}$ , was collected on high purity quartz-fiber filters (ca.  $395\ \text{cm}^2$ ) using high-volume samplers equipped with Sierra impactor inlets in accordance with IACP sampling protocols. The aerosol samples were collected for 12 hour periods (beginning at 0700h and 1900h) at three separate locations. The sampling locations in Roanoke were (1) Morningside Park (MSP), an in-town residential area, (2) the Civic Center (CIV), an in-town traffic site, and (3) Carvin Cove (CC), a rural background site. Subsequently, the EPA's Atmospheric Research and Exposure Assessment Laboratory (AREAL) selected a subset of these samples and extracted them with dichloromethane (DCM) to obtain corresponding liquid samples of extractable organic matter (EOM).

**EOM Extraction:** Aerosol sample filters and filter blanks were extracted for 21-23 hours with 150 mL of DCM in 35/45 Soxhlet extractors to separate all nonvolatile organic material for  $^{14}\text{C}$  analysis. The extracts were then filtered using  $0.2\ \mu\text{m}$  FG type Millipore filters and concentrated to less than 5 mL using rotary evaporation. After quantitatively transferring the samples to 10 mL volumetric flasks and diluting to volume with DCM, duplicate  $400\ \mu\text{L}$  gravimetric determinations were made. Aliquots of 8 mL were transferred to sample vials for carbon separation and  $^{14}\text{C}$  analysis, and the residual sample volume was archived at AREAL.

## **EXPERIMENTAL METHODS AND QUALITY CONTROL**

At NIST, Roanoke sample extracts and filter blanks extracts were characterized for their carbon

concentration, prepared as AMS targets, and then analyzed for  $^{14}\text{C}$ . To accomplish this, three separate analytical procedures were utilized.

**Carbon Separation Procedure:** Carbon in the EOM (e.g., carbon emanating from the sample and/or the DCM and filter blank) was separated from both the samples and filter blanks by evaporating the DCM solvent, followed by closed tube combustion of the carbon in the sample residue to  $\text{CO}_2$ . First, extract aliquots of 500 - 2000  $\mu\text{L}$  were quantitatively transferred to clean Vycor tubes. Filtered nitrogen gas was passed over the sample until the aliquot reached dryness. Next, a stoichiometric excess of copper(II) oxide and silver wire were added to the Vycor tube to provide oxygen for combustion and to remove oxides of sulfur. The sample tube was evacuated, sealed, and heated at 900  $^\circ\text{C}$  for 3 - 5 hours. The evolved  $\text{CO}_2$  was separated cryogenically and the mass of carbon was determined manometrically in a calibrated volume. The sample  $\text{CO}_2$  was then transferred to a sealed sample vial for storage prior to AMS target preparation. A more detailed description of the evaporation and combustion procedure can be found in Sheffield, *et al.*, (1990) and Klouda *et al.*, (1991).

The following Standard Reference Materials and reference solutions were used to validate the carbon separation procedure and to maintain quality control throughout sample processing: NIST archived DCM extracts of 1) SRM 1648, ( St. Louis Urban Particulate Matter) and 2) SRM 1650, (Diesel Soot Particulate Matter). These solutions were used to evaluate the precision of the carbon separation procedure. Triplicate analyses from single extract samples of these two SRM extracts yielded carbon concentration estimates of  $10.41 \pm 0.44$  mg/mL (sd, n = 3), and  $12.88 \pm 0.23$  mg/mL (sd, n = 3), for SRM 1648 and SRM 1650, respectively. The precision of the carbon separation procedure, in terms of the relative standard deviations was, therefore, 2 - 4 percent. These results are consistent with those reported for the Boise IACP study by Klouda, *et al.*, (1991).

To evaluate the accuracy of the carbon separation procedure, the following reference solutions, prepared in our laboratory for this study, were used:

PAH #1:  $\text{C}_{14}$  -  $\text{C}_{22}$ ,  $0.427 \pm 0.01$  mg C/mL DCM

PAH #2: C<sub>14</sub> - C<sub>24</sub>, 91.43 ± 0.21 mg C/mL DCM

Pure polycyclic aromatic hydrocarbons (PAH) were weighed and dissolved with DCM, then diluted to a known volume. The carbon concentration value was obtained by multiplying each PAH concentration by its respective percentage of carbon and summing the individual carbon concentrations. The average recovery for these reference solutions was 100.7 ± 1.6% (sd, n = 10), translating into an accuracy of 2%.

Finally, a NIST laboratory DCM Blank was processed for the purpose of evaluating the potential carbon contamination associated with the evaporation and combustion procedures. For each set of five samples, a 1 or 2 mL aliquot of High Performance Liquid Chromatography DCM was processed. These DCM aliquots spanned the volume range of the EOM extract carbon separation aliquots. The average DCM blank, normalized to 1 mL, was 2.81 ± 0.81 µg C (sd, n = 10). This is less than 2% of the sample carbon and less than 5% of the filter blank carbon processed for <sup>14</sup>C analysis.

**AMS Fe-C Target Preparation:** The final step of sample preparation was the production of an Fe-C target for AMS analysis. Target preparation was carried out in a system described by Verkouteren, *et al.*, (1987) and Verkouteren and Klouda (1991). Sample CO<sub>2</sub> was quantitatively transferred to a 6 mm OD quartz tube adapted to a vacuum manifold. The CO<sub>2</sub> from sample combustion was next reduced to graphite on iron wool at thermodynamically favorable temperatures in the presence of hydrogen and zinc, then fused into an Fe-C bead using a hydrogen-oxygen flame.

Prior to transferring sample CO<sub>2</sub> to the reduction manifold, the sample carbon was once again quantified by manometry in the reduction manifold calibrated volume. As an estimate of the sample transfer efficiency, the ratio of this carbon mass determination to that obtained from the carbon separation procedure was calculated yielding a result of 95.9 ± 5.7% (sd, n = 56). As an additional quality control check of the reduction procedure, RM 21 (<sup>14</sup>C blank graphite) was processed in parallel with the filter samples, for the purpose of estimating the level of the <sup>14</sup>C blank resulting from the target preparation and measurement processes. Additionally, the oxalic acid <sup>14</sup>C standards, SRM 4990b [HOx(I)] and 4990c [HOx(II)], processed at the same carbon mass ranges as those of the samples, were combusted and prepared as Fe-C targets.

**AMS Radiocarbon Measurement Procedures:** Accelerator mass spectrometry measurements were made

on sample Fe-C targets at the NSF-University of Arizona Accelerator Facility for Radioisotope Analysis according to the protocol outlined by Linick *et al.*, (1986) and Donahue (1991). For each 32 position target wheel, a minimum of one pair of oxalic acid radiocarbon standards [HOx(I)] and [HOx(II)] plus an RM 21 blank was measured. During each rotation of the sample wheel, individual targets were exposed to the accelerator's cesium beam for approximately 10 minutes. During this time, the  $^{14}\text{C}$  and  $^{13}\text{C}$  counts were measured by cycling between the two for 40 and 4 seconds, respectively. The number of complete wheel rotations for the Roanoke samples ranged from 3 to 6.

## RESULTS

**Fraction of Modern Carbon.** The measured  $^{14}\text{C}/^{13}\text{C}$  signal ratios of the HOx(I) and HOx(II) pairs were converted to the fraction of Modern Carbon ( $f_M$ ) according to equation 1.

$$f_M = \frac{(^{14}\text{C} / ^{13}\text{C})_{\text{HOx(II) signal}}}{(^{14}\text{C} / ^{13}\text{C})_{\text{HOx(I) signal}} * 0.95} \quad (1)$$

The resulting  $f_M$  ratio was then compared to the NIST certified value for this ratio,  $1.3406 \pm 0.0008$ , to yield the accuracy of the AMS measurements, expressed as  $\Delta\%$ . The uncertainty of the fraction of Modern Carbon for both standards and samples was based on the weighted counting statistics of the measured  $^{14}\text{C}/^{13}\text{C}$  ratio signals. The accuracy of the  $^{14}\text{C}$  measurements for the Roanoke study ranged from -0.09 to 1.4%, for targets ranging from 32 to 599  $\mu\text{g C}$ . The mass of  $^{14}\text{C}$  blank was calculated from the RM 21 data by multiplying the  $f_M$  value of RM 21 by the target carbon mass. The average mass of  $^{14}\text{C}$  contamination was  $3.9 \pm 0.7 \mu\text{g C}$  (sd,  $n = 2$ ). This calculation assumed that the contamination is modern carbon.

The fraction of Modern Carbon ( $f_M$ ) for samples was also calculated according to Eq. 1 by replacing the numerator with  $(^{14}\text{C}/^{13}\text{C})_{\text{sample signal}}$ . The uncertainty of the calculated sample  $f_M$  was derived by propagation of the errors (see Ku, 1966) of the measured  $^{14}\text{C}/^{13}\text{C}$  ratio signal of the sample and its associated

HOx(I) standard. The precision of the  $f_M$  results for all samples and blanks was 2% or less.

**Blank Corrections.** Before these  $f_M$  results can be used to model atmospheric concentration, a correction for filter blank contributions must be made and a confidence interval estimated. The correction for filter blank carbon contributions to the mass and  $f_M$  of a sample was calculated according to Eq. 2, where the mean value of the filter blank mass of carbon and  $f_M$ , corresponding to the sample extract set (1 or 2) was used.

$$f_M (Corr.) = \frac{f_{M(measured)} - (\phi_{fb} * f_{M(fb)})}{1 - \phi_{fb}} \quad (2)$$

where:

$$\phi_{fb} = \frac{\text{mass fb C}}{(\text{mass sample C} + \text{mass fb C})}$$

The mean filter blank mass and  $f_M$  for extract set 1 was  $69.7 \pm 33.0 \mu\text{g C}$  and  $0.54 \pm 0.12$  (sd, n= 6), respectively, yielding relative standard deviations of 47% and 22%. Additionally, we noted a linear correlation between these two variables. The mean filter blank mass and  $f_M$  of extract set 2 was  $27.1 \pm 4.7 \mu\text{g C}$  and  $1.22 \pm 0.35$  (sd, n = 3), yielding relative standard deviations of 17% and 29%, respectively.

Conventional error propagation to estimate uncertainties is a reliable method to propagate errors through linear functions. When functions are non-linear, such as Eq. 2, and relative errors of the variables are small, an approximate solution can be obtained by expanding the function using a Taylor's series and assuming that only the lower order terms are necessary to describe the function. This assumption breaks down when the relative errors of a variable are large, particularly if they are associated with the non-linear portion of the function, as is the case for the Roanoke filter blanks. These errors could be evaluated by expanding the Taylor series function to include higher order terms, however, this would result in a very complicated function. Instead, Monte Carlo error propagation simulations were used to calculate the uncertainties and construct

approximate 90% confidence intervals for the Roanoke  $f_M$  (Corr.) data. The results from these simulations yielded asymmetric confidence intervals for  $f_M$  (Corr.) in which the width ranged from 0.03 to 0.67. (Note: confidence intervals routinely calculated as  $CI = \bar{x} \pm t_{\alpha} * \hat{\sigma}$  yield confidence intervals symmetric about the estimated value of  $\bar{x}$ .) We have chosen an approximate 90% confidence interval width of 0.30 as a cut off beyond which the results may not be useful for further modeling of the  $^{14}\text{C}$  contribution to the EOM in Roanoke. Seven of the filter samples fell within this category. Two additional samples may also not be useful for modeling calculations because the recovered carbon mass was inconsistent (e.g., too high or too low) with the EOM mass data. The results of the  $f_M$  (Corr.) calculation and error propagation are presented in Figure 1. The nine samples discussed above are indicated by dashed lines or asterisks. The results are summarized by sampling site and time.

**Residential Wood Combustion (RWC) Contribution:** Roanoke, VA is assumed to have three major carbon based emission sources: 1) residential wood combustion (biogenic carbon), 2) motor vehicle exhaust (fossil carbon), and 3) residential heating oil combustion (fossil fuel). The two fossil sources cannot be distinguished by  $^{14}\text{C}$  analysis and thus, the model reduces to two components; biogenic and fossil carbon. To estimate the relative source contributions, blank-corrected  $f_M$  results [ $f_M$  (Corr.)] were normalized to the  $^{14}\text{C}$  abundance of the average age of wood burned during the Roanoke IACP sampling period. Our estimate of the average age of wood burned in Roanoke during the winter of 1988-89 was 30 - 60 years. The relative contribution of RWC to the EOM fraction, is given as  $f_{RWC}$  according to Eq. 3:

$$f_{RWC} = (f_M \text{ EOM}) / (f_M \text{ WOOD}) \quad (3)$$

Note that the calculation of RWC is a systematic correction to the sample  $f_M$  (Corr.) value, which depends on the value chosen for  $f_M$  Wood. Using an equal mass tree ring model, the  $f_M$  value for wood between 30 - 60 years is 1.19 - 1.40. ( see Klouda, *et. al.*, 1991). The  $f_M$  value for an average age of 45 years is 1.26. Thus, the conversion of  $f_M$  (Corr.) to RWC adds an additional uncertainty to the  $f_M$  (Corr.) values of 8 to 11%.

## CONCLUSIONS

Radiocarbon measurements were made on twenty nine EOM sample extracts and nine filter blanks separated from fine particle filters collected in Roanoke, VA during the winter of 1988 -1989. The fraction of Modern Carbon was calculated from the measured  $^{14}\text{C}/^{13}\text{C}$  signal ratios of the sample and its associated oxalic acid radiocarbon standard (SRM 4990b). All sample  $f_M$  values were corrected for filter blank contributions to the carbon mass and fraction of Modern Carbon. Monte Carlo error simulations were employed to estimate the uncertainty of the blank corrected fraction of Modern Carbon because of the large relative errors in the mean values of the filter blank mass and fraction of modern carbon. A total of seven samples have approximate 90% confidence interval widths that exceed 0.30. Further use of the data from these seven samples requires rigorous evaluation of the error imparted by these large confidence intervals. Nevertheless, the results indicate that residential wood combustion was the dominant source of atmospheric aerosols EOM for both the day and night at the residential site (Morningside Park) and the rural background site (Carvin Cove). The traffic site (Civic Center) yielded lower  $f_M$  (Corr.) values overall, due mainly to the impact of motor vehicle emissions. Additionally, the  $f_M$  (Corr.) data suggest that on average, the nighttime samples have higher concentrations of  $^{14}\text{C}$ . Use of these results to model modern carbon contribution to the EOM fraction in Roanoke are reported elsewhere in these proceedings, Lewis, *et al.*, (1993).

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# Roanoke, VA Winter of 1988 - 1989

Blank Corrected Fraction of Modern Carbon by Site and Time  
at the Approximate 90% Confidence Interval

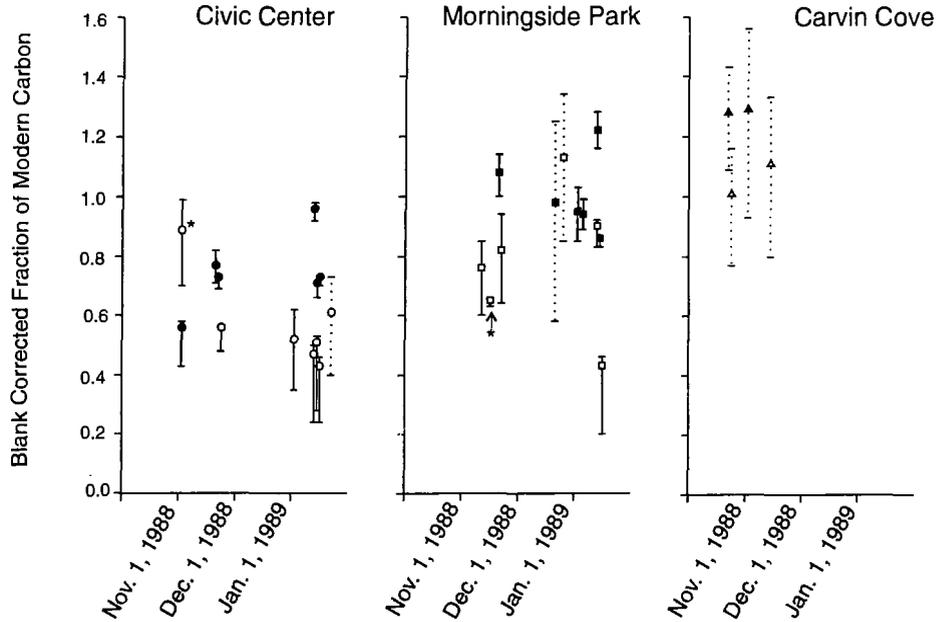


Fig. 1: Blank corrected fraction of Modern Carbon in Roanoke VA., during the winter of 1988 - 1989. Open symbols represent daytime samples. Filled symbols represent nighttime samples. Error bars represent the approximate 90% confidence interval. Note the asymmetry of the confidence intervals. Those samples indicated by dotted lines have confidence interval widths that exceed 0.30. Further use of these data require rigorous attention to the error structure (see text for details). Two additional samples, indicated by asterisks, are also not suggested for further use because of inconsistencies between the EOM and carbon mass results.

**SOURCE APPORTIONMENT OF FINE PARTICLE ORGANICS  
AND MUTAGENICITY IN WINTERTIME ROANOKE**

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**ABSTRACT**

During the 1988-1989 winter the U.S. EPA conducted a comprehensive field study in Roanoke VA as part of its Integrated Air Cancer Project (IACP). This paper presents results of the source apportionment of fine particle extractable organic matter (EOM) and its associated mutagenicity (*Salmonella typhimurium* TA98 +S9 and TA98 -S9). The source apportionment methodology is based on multiple linear regression (MLR) using a variety of tracer species: <sup>14</sup>C, metallic elements and volatile hydrocarbons (VHC) whose ambient concentrations were measured simultaneously with the EOM and mutagenicity. The results are compared with those from previous IACP studies in other locales.

**INTRODUCTION**

As part of the IACP the U.S. Environmental Protection Agency has conducted a series of wintertime field studies in U.S. cities to measure ambient concentrations of fine particle EOM and associated mutagenicity. Receptor modeling has been employed with these measurements to determine the quantitative contributions of various emissions sources to both EOM and mutagenicity. The present work gives receptor modeling results for the 1988-1989 field study in Roanoke VA, an airshed whose principal sources of ambient EOM were anticipated to be woodsmoke, mobile sources and residential distillate oil combustion (RDOC).

**EXPERIMENTAL**

Overviews of the Roanoke ambient field sampling program have been given<sup>1,2</sup>. The results that follow are from analyses of 12-h fine particle (0 - 2.5  $\mu$ m dia) and VHC samples collected simultaneously at the two primary sites -- Morningside Park (residential site) and Civic

Center (roadway site). The analyses followed previous IACP procedures and generated an ambient data set of the following parameters: elemental composition of fine aerosol from x-ray fluorescence (XRF)<sup>3</sup>; fine EOM from dichloromethane Soxhlet extraction<sup>3</sup>; TA98 +S9 and TA98 - S9 mutagenicities of the EOM from plate incorporation bioassays<sup>3</sup>; <sup>14</sup>C content of the EOM from accelerator mass spectrometry<sup>4</sup>; and VHCs from gas chromatography-flame ionization detection<sup>5</sup>.

#### MLR RECEPTOR MODELING

The same MLR modeling approach was used as in earlier IACP work. The measured concentration of the pollutant of interest (i.e., EOM or mutagenicity) is represented by a sum of individual source contribution terms, with each term being the product of the measured concentration of a tracer species for that source and an initially unknown coefficient that is subsequently determined by an MLR calculation. A non-zero intercept is allowed for, which can be regarded as the average contribution of additional sources not represented in one of the explicitly identified source terms.

In previous IACP work the concentration of fine-particle Pb was used as a mobile-source tracer. In recent years, however, this has become less tenable, because of the phaseout of leaded gasoline. During the preceding IACP study in Boise -- while Pb was still a satisfactory tracer -- the use of any one of several VHC species as tracers was shown to give estimates for the mobile source contribution which were virtually identical to those produced with Pb<sup>6</sup>. For the Roanoke data however the VHC species were clearly superior to Pb, as judged from the quality of the MLR fits that could be achieved (largest r<sup>2</sup> value). The unimpressive Pb-Br correlation (r<sup>2</sup> = 0.65) exhibited by the Roanoke data also suggested that Pb was not a reliable mobile source tracer. Consequently, the VHC species 2-methylhexane (2MeHx) was used instead of Pb in the present work, as it produced a slightly better MLR fit than the other VHCs.

Fine particle soil-corrected potassium (K') has proven to be very useful as a woodsmoke tracer in previous IACP work. In the planning stage of the Roanoke project, it was conjectured that K' might serve as a tracer of overall residential heating. This was because RDOC as well as wood combustion were anticipated to be important contributors to ambient EOM concentrations, and the expected similar diurnal emission patterns of these two source categories would frustrate their separate estimations by an MLR technique. As shown below however RDOC was so small in comparison to wood combustion that K' retained the same role for Roanoke as it had in previous IACP work. Ondov et al.<sup>7</sup> report a similarly small estimate of the RDOC contribution, through use of an enriched isotope of samarium as an intentional tracer.

#### RESULTS

##### Modeling

Multiple linear regression of the measured concentrations of EOM ( $\mu\text{g m}^{-3}$ ) and R<sub>98+</sub> and R<sub>98-</sub> mutagenicities (revertants m<sup>-3</sup>) resulted in the following equations:

$$[\text{EOM}]_i = (40 \pm 3)[\text{K}']_i + (656 \pm 83)[2\text{MeHx}]_i - 0.3 \pm 0.7 \quad (1)$$
$$r^2 = 0.92, \quad n = 40;$$

$$[R_{98+}]_i = (32 \pm 6) [K']_i + (1960 \pm 140) [2MeHx]_i + 2.6 \pm 1.1 \quad (2)$$

$$r^2 = 0.92, \quad n = 37;$$

$$[R_{98-}]_i = (21 \pm 4) [K']_i + (1100 \pm 130) [2MeHx]_i + 4.2 \pm 0.9 \quad (3)$$

$$r^2 = 0.86, \quad n = 38.$$

The units of the tracer concentrations  $[K']$  and  $[2MeHx]$  are  $\mu\text{g m}^{-3}$  and ppmC, respectively, and

$$[K'] = [K] - (0.22 \pm 0.01) [Fe]. \quad (4)$$

The numerical coefficient in equation 4 is the average potassium-to-iron ratio measured in the coarse-particle (2.5 - 10  $\mu\text{m}$  dia) fraction, as done previously<sup>3</sup>.

The cases used in each of the three fits were approximately equally divided between the Civic Center and Morningside Park sampling sites, and between day and night. The quality of the fits, as judged by the  $r^2$  values, were similar to or better than those achieved in the three earlier IACP studies, each of which involved approximately the same number of cases as in the present study.

Table I shows the average source contributions to the measured concentrations of EOM and mutagenicity, averaged over both sampling sites as well as day and night. The source contributions were calculated by inserting the averages of the measured values of  $[K']$  and  $[2MeHx]$  into equations 1 - 3. Table I also gives the calculated mutagenic potency of the EOM associated with each source. The source potency (revertants  $(\mu\text{g EOM})^{-1}$ ) is simply the ratio of the R to EOM regression coefficient for that source. For comparison Table I also includes corresponding results from the three earlier studies (Boise, Albuquerque and Raleigh). The latter results are from Lewis et al.<sup>3</sup>, which gives references to the original work. It is important to note that the source potency values listed in Table I are derived entirely from ambient measurements.

#### Validation by <sup>14</sup>C

Since <sup>14</sup>C is absent from fossil fuels, its presence in fine particle atmospheric samples is a direct (non-statistical) indication of the contribution of contemporary carbon sources, assumed to be essentially only residential woodburning in the wintertime Roanoke airshed. The <sup>14</sup>C-derived estimate of woodsmoke EOM concentration in a sample  $i$  is given by

$$[\text{Woodsmoke EOM}]_i = [\text{EOM}]_i (f_{RWC})_i \quad (5)$$

with  $f_{RWC}$  being the fraction of residential wood combustion carbon in the sample. On the other hand the term in equation 1 involving  $[K']_i$  is an independent statistical estimate of the same quantity. Thus the right side of equation 5 and  $[K']_i$  should be linearly related, with a slope that is the same as the regression coefficient for  $[K']$  in equation 1, and with no intercept. Figure 1 shows  $[\text{EOM}]_i * (f_{RWC})_i$  values for all available data ( $n = 20$ ) recommended for use by Klinedinst et al.<sup>4</sup>, plotted vs  $[K']$ . The straight line in the figure is the product of  $[K']$  and its regression coefficient from equation 1, with the dotted band representing the coefficient's uncertainty.

For the most part the points in Figure 1 cluster around the line, showing that the potassium-traced portion of EOM is wood combustion-related, and indicating by inference that the RDOC portion must be small in comparison. This conclusion is also supported by a Roanoke TSP emissions inventory specific to the 1988-1989 wintertime period of the IACP field study which indicates an RDOC emissions rate that is only a few percent of that for wood combustion<sup>8</sup>.

#### CONCLUSIONS

The Roanoke results presented in this paper together with corresponding results from the previous IACP studies (Table I) show some very clear consistencies across four geographically scattered U.S. airsheds: (1) ambient EOM is dominated by woodsmoke, rather than mobile sources emissions, for these wintertime studies; (2) the mutagenic potency (*Salmonella typhimurium* TA98 +S9) of ambient woodsmoke is approximately 1 revertant per microgram of EOM; (3) the mutagenic potency of ambient mobile source emissions is about three times that of woodsmoke. These consistencies span a period of four years, and depend neither on the type of wood used nor on the choice of a mobile source tracer (particulate Pb or volatile hydrocarbons). The use of <sup>14</sup>C measurements have served to confirm the MLR-based apportionment of EOM.

The woodsmoke domination of EOM may not be surprising for Albuquerque and Raleigh, since the sampling site for both was in a residential neighborhood. For Boise and Roanoke however the results come from the combining of measurements at both residential and roadway sites, and woodsmoke still dominates EOM overall. The choice of sampling site locations within the cities presumably had little effect on the potency values that were obtained.

The Roanoke results for TA -98 mutagenicity and potency are the first known ambient-derived values for these parameters.

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#### DISCLAIMER

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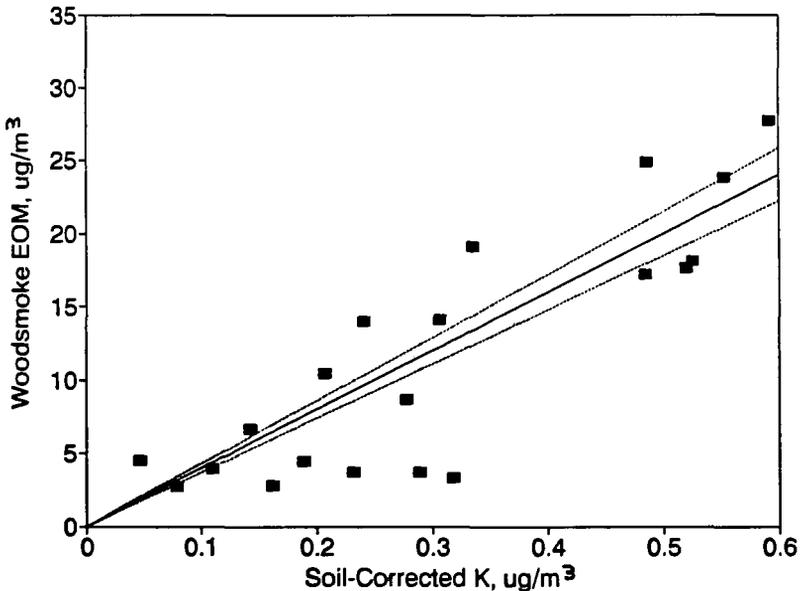


Figure 1. <sup>14</sup>C-determined extractable organic matter vs soil-corrected potassium. The straight line and its uncertainty band is given by  $(40 \pm 3) [K']$ , from equation 1.

TABLE I Average ambient concentrations (EOM, TA98 +S9, and TA98 -S9) and mutagenic potencies attributed to woodsmoke and mobile sources in four U.S. cities during wintertime. The apparent relative importance of the sources depends on the the location of sampling sites within each city and season, and are not necessarily representative of annual city-wide ratios. Non-Roanoke results are from Ref. 3.

	Woodsmoke	Mobile Sources	Intercept	Meas. Total
Roanoke VA (1988-89) <sup>d</sup> n = 37 - 40				
EOM Conc'n <sup>a</sup>	8.1 ± 0.6	4.0 ± 0.5	-.3 ± .7	12
R <sub>98+</sub> Conc'n <sup>b</sup>	5.9 ± 1.1	10 ± 1	2.6 ± 1.1	19
R <sub>98+</sub> Potency <sup>c</sup>	0.80 ± .16	3.0 ± 0.4	---	---
R <sub>98-</sub> Conc'n <sup>b</sup>	4.5 ± 0.9	5.8 ± 0.7	4.2 ± 0.9	15
R <sub>98-</sub> Potency <sup>c</sup>	0.53 ± .11	1.7 ± 0.3	---	---
Boise ID (1986-87) <sup>d</sup> n = 40				
EOM Conc'n <sup>a</sup>	14 ± 2	6 ± 2	2 ± 2	22
R <sub>98+</sub> Conc'n <sup>b</sup>	12 ± 3	18 ± 3	3 ± 4	32
R <sub>98+</sub> Potency <sup>c</sup>	0.84 ± .25	3.0 ± 1.1	---	---
Albuquerque NM (1984-85) <sup>e</sup> n = 44				
EOM Conc'n <sup>a</sup>	15 ± 1	3 ± 1	1 ± 1	19
R <sub>98+</sub> Conc'n <sup>b</sup>	19 ± 2	11 ± 3	3 ± 3	32
R <sub>98+</sub> Potency <sup>c</sup>	1.3 ± .2	3.7 ± 1.5	---	---
Raleigh NC (1984-85) <sup>e</sup> n = 40				
EOM Conc'n <sup>a</sup>	16 ± .5	1 ± .3	0.1 ± 1	17
R <sub>98+</sub> Conc'n <sup>b</sup>	12 ± 1	4 ± 1	1 ± 1	18
R <sub>98+</sub> Potency <sup>c</sup>	0.78 ± .07	3.7 ± 1.5	---	---

<sup>a</sup> μg / m<sup>3</sup>

<sup>b</sup> revertants / m<sup>3</sup>

<sup>c</sup> revertants / μg EOM

<sup>d</sup> residential and roadway site

<sup>e</sup> residential site only

## COMPARISON OF RESIDENTIAL OIL FURNACE AND WOODSTOVE EMISSIONS

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### ABSTRACT

This paper compares the emissions from residential oil furnaces and residential woodstoves. The comparison is based on a number of analyses that were performed on the emissions, including total mass, filterable particulate, total extractable organics, and mutagenicity. The emission samples were gathered as part of the Integrated Air Cancer Project and included the field testing of oil furnaces in Roanoke, VA, during the 1988-89 winter; field testing of woodstoves in Boise, ID, during the 1986-87 winter and laboratory tests to support both field studies. The results show that woodstoves produce higher emissions than even poorly tuned oil furnaces. Mutagenicity of emissions from both types of heating systems is about the same on a revertants per microgram basis but, because of their much higher emission rate, woodstoves have a higher mutagenic potential on a per hour of operation basis and per unit heat input in the fuel. Although there are 2-3 times more oil furnaces in use in the U.S. than woodstoves, of the two, woodstoves still have a higher mutagenic potential.

### INTRODUCTION

Consumption of wood as a home heating fuel declined markedly during the early decades of the 20<sup>th</sup> century as it was displaced by coal which was then displaced by fuel oil. In the last 20 years, fuel oil has itself been displaced in many homes by natural gas, so that more than half of all homes are heated with natural gas. Electrical heating ranks second, followed by fuel oil and lastly wood. Wood consumption increased markedly during the 1970s with the sharp increase in fossil fuel prices. Although some wood burners have tired of using wood there continues to be a market for about 200,000 new stoves each year. In addition, fireplaces continue to have widespread appeal; approximately 60% of all new homes built today have a fireplace. Adding a fireplace is one of the most cost effective renovations one can make to a home.

This paper presents results of continuing work performed under the aegis of EPA's Integrated Air Cancer Project (IACP) to characterize and compare air emissions from combustion of wood and fuel oil for residential heating. This paper emphasizes the analyses of stack emission samples collected from oil furnaces in Roanoke, VA, during the IACP's winter 1988-89 field study and supporting oil furnace and woodstove laboratory projects.

### EXPERIMENTAL APPROACH

## Roanoke, VA, Oil Furnaces

Ten homes with oil furnaces in Roanoke, VA, were selected for source testing. Although a cross section of furnace technologies was desirable, primary emphasis was on pairing each home with an oil furnace (and not using wood heat) to a non-oil non-wood heated home in the same neighborhood. Furnace performance was measured using standard procedures employed by furnace repair firms.

### Laboratory Oil Furnace

A single Williamson residential oil furnace was tested in the laboratory, first with an old technology (pre-1970) atomizing gun burner and then with a modern retention head burner. The furnace and burners have been described previously<sup>1</sup>

### Laboratory Woodstoves

Two woodstoves were tested at EPA's woodstove test facility at the Environmental Research Center, Research Triangle Park, NC. One was a conventional, uncontrolled Lopi model 330/440, and the other was a low emission noncatalytic Lopi model Answer. The latter stove was certified to EPA's Phase 1 emission standard.

### Emission Sampling Equipment

The basic device used for air emission sampling was the Source Dilution Sampler (SDS) which has been described previously<sup>2,3</sup>. For the experiments reported here the basic sampler was modified to include:

- A cyclone located just before the SDS filter designed to remove particles  $>2.5 \mu\text{m}$  aerodynamic equivalent diameter
- Two fine particle samplers in parallel which extract a 4 lpm slip stream of the diluted stack sample just ahead of the SDS filter. They are identical except that one uses a Teflon<sup>®</sup> filter and the other a quartz filter for elemental/organic carbon and trace metals, respectively. Both samplers have a cyclone ahead of the filter to remove particles  $>2.5 \mu\text{m}$ .
- A sampler which extracted a 0.15 lpm sample of the diluted gas just ahead of the SDS filter for aldehyde analysis. The sample was collected in cartridges containing dinitrophenylhydrazine (DNPH) coated silica gel.
- An evacuated canister which extracted a 0.5 lpm slip stream between the SDS filter and XAD-2 cartridge for hydrocarbon analysis.

A block diagram of the sampler with these modifications is shown in Figure 1.

In Roanoke, sampling was conducted at each home for 4 days starting Saturday at 7 am and ending Wednesday at 7 am. The 4 days were further divided into eight 12-hour sampling periods representing daytime (7 am - 7 pm) and nighttime (7 pm - 7 am). In some cases, results are presented as weekday daytime, weekday nighttime, weekend daytime, and weekend nighttime averages.

## RESULTS

### Roanoke, VA, Oil Furnaces

The furnace model and burner information, stack carbon dioxide (CO<sub>2</sub>) and Bacharach smoke number taken before the barometric damper are shown in Table I. No adjustments were made to the furnaces; however, homeowners were advised if the furnace appeared to need adjustment.

Chimney exit total extractable organic emissions for each Roanoke home are presented in Table II. In Table II the results have been aggregated into weekday daytime and nighttime and weekend daytime and nighttime averages. Also included is the average percent of time the furnace was on (burner running) for each aggregated sample period. The emission results are calculated on the basis of the total sample period, not just the time the burner was on.

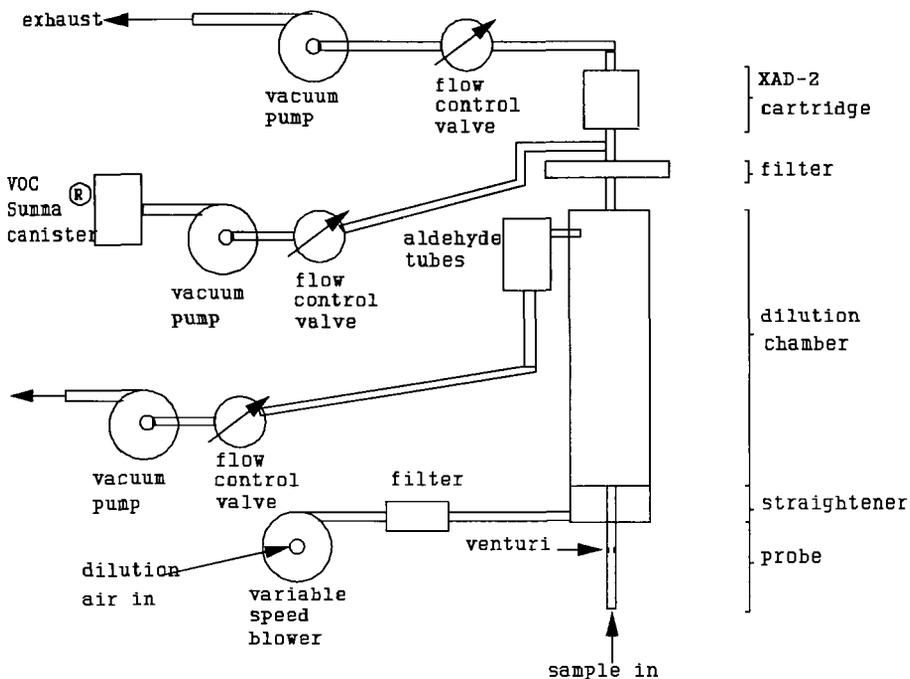


Figure 1. Block diagram of source dilution sampler (SDS).

#### Laboratory Oil Furnaces

The majority of the laboratory oil furnace test results have been published previously<sup>1</sup>. There was a general correlation between smoke number and emission rate. Even under best tuned conditions the old style burner's emissions were 2-4 times higher than those of the new technology burner. The old burner's emissions consisted of about equal parts of organic and elemental carbon whereas the new burner's emissions consisted of 20 parts organic carbon to 1 part elemental carbon. Bioassay results using the microsuspension assay<sup>4</sup> showed that potency ranged from 7 to 18 revertants/microgram (rev/ $\mu$ g) of organic for both burners. Because the retention head burner emitted substantially less extractable organics per hour, its mutagenic emission rate was 0.006 rev/J heat input compared to 0.02 rev/J for the old style burner.

#### Laboratory Woodstoves

Laboratory and field woodstove test results have been widely

Table I. Summary of furnaces tested in Roanoke, VA, IACP field study.

Residence	Furnace description	Stack gases, %		Bacharach smoke number	Stack draft, in. H <sub>2</sub> O <sup>a</sup>	Efficiency, %
		CO <sub>2</sub>	O <sub>2</sub>			
R01	Climate Control, burner model 72-6, 30 yrs old, 1.27 MJ Rating	6.3	12.5	3-4	0.04	76.2
R04	(no model data), 40 yrs old, 4.2 L/hr fuel nozzle	8.5	8.0	0	0.10	- <sup>b</sup>
R07	Lennox model CC-358-363, burner model LDI-75, 40 yrs old	8.3	9.8	1-2	0.03	79.2
R10	Homart furnace and burner, >30 yrs old	7.5	10.3	10	0.05	71.0
R13	Mueller Climatrol model 227-110, burner model 487-75, >30 yrs old, 9.3 MJ rating	9.0	8.8	2	0.03	74.0
R16	ARCO Flame model AI-3, no burner model No.	7.5	11.0	5	0.045	70.5
R19	Kewanee model VT-510, Series 2X, burner Petro model P-9-70-KA, installed in 1951	8.3	9.6	2-3	0.04	79.5
R22	Hell, burner Wayne model M-SR, 1.1 MJ rating, new furnace	12.5	4.2	<1	0.03	81.5
R25	Airtemp, burner model 5813-1, 3.8 L/hr fuel nozzle, 20 yrs old	9.0	9.5	<1	0.03	72.2
R28	Mueller Climatrol, burner model 88-88, 2.5 L/hr fuel nozzle	6.5	12.6	1-2	0.05	67.0

a One inch of water pressure = 249 Pa  
 b Insufficient data to calculate efficiency

reported<sup>5,6,7</sup>. The current work can best be compared to a laboratory study<sup>7</sup> supporting the IACP field study in Boise, ID. The combined Boise and Roanoke laboratory woodstove results for total SDS train catch are shown in Figure 2. All of the conventional stove data (with the exception of one data point) follow the expected trend - higher emissions as burnrate decreases below 2-2.5 kg/hr. Both of the low emission stoves produced lower emissions compared to the conventional stove. They also exhibited a narrower burnrate range. Emission of aldehydes (available for Roanoke woodstoves only) showed a trend of increasing emission rate with increasing burnrate. The range was from 0.1 to 0.5 g/hr total aldehydes. Formaldehyde was the largest fraction (37%) followed by acetaldehyde (20%).

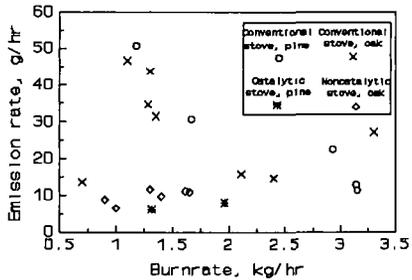


Figure 2. Total SDS emissions.

The mutagenic potential (plate incorporation assay, TA98+S9) of the Boise and Roanoke woodstove SDS filter (particle bound) catch results is shown in Figure 3. One can draw the conclusion that emissions from burning pine are much more mutagenic than emissions from burning oak. There also appears to be a trend of increasing

Table II. Total extractable organics in samples from Roanoke, VA, oil furnaces.

Residence	Emission rate, g/hr (burner on time, %)			
	weekend day	weekend night	weekday day	weekday night
R01	1.90 (17.3)	1.37 (17.3)	no sample <sup>a</sup>	no sample <sup>a</sup>
R04	4.63 (19.8)	2.66 (29.7)	3.45 (18.6)	5.67 (43.6)
R07	0.85 <sup>b</sup> (46.7)	1.02 <sup>b</sup> (46.7)	1.02 <sup>b</sup> (46.7)	1.79 <sup>b</sup> (46.7)
R10	0.85 <sup>b</sup> (46.7)	1.28 <sup>b</sup> (46.7)	9.05 <sup>b</sup> (46.7)	1.04 <sup>b</sup> (46.7)
R13	1.20 <sup>b</sup> (47.8)	0.99 <sup>b</sup> (34.1)	1.54 (40.5)	1.47 (48.3)
R16	1.97 <sup>b</sup> (35.6)	1.83 (38.8)	1.94 (47.2)	6.21 (53.4)
R19	1.71 <sup>c</sup> (84.3)	1.22 (44.4)	1.81 (77.9)	3.42 (57.6)
R22	1.13 (24.3)	1.17 (24.3)	0.69 (24.3)	1.13 (24.3)
R25	4.17 (35.7)	3.92 (13.0)	3.30 (22.8)	3.83 (6.8)
R28	6.01 (72.6)	5.11 (79.4)	2.44 (54.8)	4.00 (83.8)

a Samples lost

b Filter samples lost

c XAD-2 total chromatographable organics sample lost

potency with increasing burnrate, especially when burning pine. This trend has been noted previously<sup>5</sup>. Similarly, a trend of increasing polycyclic aromatic hydrocarbons (PAH) emission rate with burnrate was seen again which correlates well with the mutagenic potential trend if it is assumed that most of the mutagenicity is caused by the PAHs.

Comparison of Woodstove and Oil Furnace Emissions

Comparing total SDS emissions in Figure 2 and Table II, one can see that the conventional woodstoves emission rate is 5-20 times higher than the emission rate for oil furnaces. Emission rates from low emission woodstoves are 2-5 times higher than for oil furnaces. The dominant component of oil furnace organic emissions is unburned fuel oil, whereas wood smoke consists of a very broad mixture of organic compounds. For this comparison the woodstove data in Figure 2 were reduced by 20% to arrive at an approximation of the extractable organic fraction.

A comparison of overall average woodstove and oil furnace emission mutagenic factors<sup>1</sup> (microsuspension assay) yielded:

- conventional woodstove average 0.6 rev/J fuel energy input
- low emission woodstove average 0.1 rev/J fuel energy input

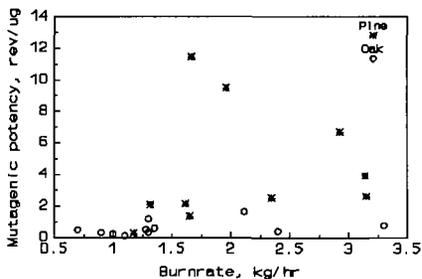


Figure 3. Mutagenic potency.

old technology oil burner 0.02 rev/J fuel energy input  
new technology oil burner = 0.006 rev/J fuel energy input

#### SUMMARY AND CONCLUSIONS

Total SDS emission rates from woodstoves vary from as low as 5 g/hr for low emission stoves to as high as 50 g/hr for a conventional stove. Emission rates from Roanoke residential oil furnaces tested with the same sampling train ranged from 0.85 to 6 g/hr.

Aldehyde emissions from woodstoves ranged from 0.1 to 0.5 g/hr, increasing with increasing burnrate.

On the basis of equal heating value, the conventional woodstove mutagenic emission factor is about 30 times higher than the one for old technology oil furnaces and about 100 times more mutagenic than the one for new technology retention head oil burners. The mutagenic emission factor for new, low emission woodstoves is about 5 times higher than the one for old technology oil burners and about 20 times higher than the factor for new technology retention head oil burners. Further analyses are underway to determine the carcinogenicity of oil furnace emissions.

#### ACKNOWLEDGEMENTS

R.K. Stevens, C.W. Lewis, and J.O. Baugh, all of the Atmospheric Research and Exposure Assessment Laboratory, specified the design of the source signature samplers, assisted during their initial setup, and provided the reduced data from the samples collected. D.F. Natschke, Acurex Environmental Corp., oversaw the laboratory studies, providing sample recovery and analysis of samples from the SDS and final reports from each test series.

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***Session 6***  
***Indoor Air Quality in***  
***Highly Confined Environments***

## STRATEGIES USED TO MANAGE AIR QUALITY IN MANNED SPACECRAFT

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### ABSTRACT

The quality of respirable air in crew compartments has been a concern since the earliest days of manned space flight. Air contaminants are controlled by limiting the offgassing of flight hardware and by removing contaminants using high-capacity air revitalization systems. Air quality has been monitored retrospectively by ground-based analysis of samples obtained during flights; however, on-board instruments are under development to measure contaminants during flight. This requires that spacecraft maximum allowable concentrations (SMACs) be established for brief and long-term exposures so that appropriate actions can be taken promptly when contaminants exceed those limits.

At present, SMACs are being set for chemical exposures ranging from 1 hour to 180 days using a scientific approach developed in cooperation with the National Research Council. Original toxicity studies are reviewed for quality and completeness and all toxic effects induced by a chemical are analyzed to determine the most sensitive effect. Human inhalation data are preferred, but often extrapolations must be made from animal data, from noninhalation data, or by structure-activity analysis. In addition, the biological changes caused by space flight, including loss of red cell mass, changes in immune function, and cardiac dysrhythmias, are factored into the analysis. The approach is illustrated by describing the results for indole, Freon 113, and octamethyltrisiloxane (OMTS).

### INTRODUCTION

Air that is safe to breathe is the most immediate environmental need of space crews. NASA has learned several important lessons about managing air quality during its experience with manned space exploration. Chemically induced illness in test subjects during a closed environmental test led to strict controls on the chemicals used to clean interiors and the products permitted to offgas into the closed environment<sup>1</sup>. Review of the cause of the tragic ground fire during the testing of Apollo 1 resulted in stricter controls on flammability of materials and reduction of the oxygen percentage of the atmosphere in spacecraft<sup>2</sup>. The value of redundancy was underscored during the flight of Apollo 13 when explosion of an external oxygen tank resulted in the potential for accumulation of life-threatening concentrations of carbon dioxide. Only an unplanned "jury rig" of the Command Module's carbon dioxide removal system enabled the crew to maintain a safe atmosphere in the lunar module, where they had taken refuge, until an Earth landing could be executed<sup>2</sup>. The historic Apollo-Soyuz mission nearly ended in tragedy for the American crew because of entry of toxic propellants (nitrogen dioxide and possibly methylhydrazine) into the cabin during descent through the Earth's atmosphere<sup>3</sup>. The design of modern spacecraft and operational procedures after extravehicular activity (EVA) minimize the risk of crew exposure to propellants. The most serious air-quality risk in modern spacecraft is the potential for thermodegradation of polymers associated with electrical hardware. The most significant of these occurred aboard the Shuttle in June 1991 when a refrigerator motor overheated and caused the release of formaldehyde and ammonia into the crew compartment. More thermal-overload protection has been placed on electrical motors since this incident.

The Russian experience with air-quality problems is not as well known to us as the NASA experience; however, there are several interesting references to problems they have encountered<sup>4</sup>. During a 150-day mission on Salyut 7 (an early space station), a problem in the air revitalization system was believed to have generated "acrid odors" that nearly exceeded the crew's ability to tolerate them. During 140 and 175-day missions cosmonauts were reported to have developed sensitivity to formaldehyde. The authors concluded that formaldehyde concentrations in cabin atmospheres needed to be reduced.

The incidents listed above illustrate that air contaminants can originate from a variety of sources and that unexpected releases must be anticipated. Chemical contamination routinely enters the spacecraft air from hardware offgassing, use of utility chemicals, and metabolism of the crew. As a result of accidents, chemicals can originate from payload experiments, fluid systems, thermodegradation of electrical devices, anomalies in the air revitalization system, and entry of chemicals that are normally present outside the spacecraft (propellants). In the past, strategies to manage these risks have depended heavily on Earth-based resources; however, as missions lengthen and become more remote from Earth, the resources to manage air quality problems must be available on the spacecraft. A major part of this strategy is on-board monitoring of air contaminants and the setting of contaminant limits that address both short- and long-term exposures. The overall strategy of air quality management will be described first, then the focus will be shifted to methods available to set contaminant limits for spacecraft air.

## **STRATEGY FOR CONTROL OF AIR CONTAMINANTS**

NASA uses five steps to manage air quality in spacecraft; the steps limit known risks to air quality, but also recognize the need to be prepared for unexpected releases.

### **Offgas Testing of Hardware and Materials**

The risk of air contamination is severely limited by offgas testing of all nonmetallic hardware and materials that constitute the cabin interior. Test items are warmed in a sealed chamber for 72 hours at 120 °F and all volatile contaminants released into the test chamber are analyzed by gas chromatography and mass spectrometry (GC/MS). No item may release contaminants that collectively exceed a total toxicity value of 0.5. Total toxicity value (T value) is defined as the sum of the ratio of each contaminant concentration (indexed to the spacecraft volume in which it will be used) to its 7-day SMAC. Space modules are also assessed by mathematically summing the individually-measured products from all hardware in that module and by measuring contaminants released inside the assembled module before launch. Typically, the mathematical assessment of a module gives T values an order of magnitude greater than the T values measured in the module before launch.

### **Containment of Hazardous Chemicals**

NASA classifies the toxic hazard from a chemical into one of three categories. The lowest category is called a nonhazard and would allow no more than mild, transient eye irritation that does not require therapy. A critical hazard is one that could cause up to moderate eye irritation, can last longer than 30 minutes, and may require therapy, but is unlikely to cause lasting eye damage. Finally, a catastrophic hazard is one that poses a risk of permanent eye damage, systemic toxicity that impairs performance of the mission, or delayed serious injury. NASA requires that experiments or systems that pose a critical hazard must have single-fault-tolerant containment and those that pose a catastrophic hazard must have double-fault-tolerant containment. Building fault tolerance into hardware can be expensive and consumes valuable weight and volume resources. Hence, the toxicological assessments must not be overly conservative.

### **Air Revitalization Systems**

Spacecraft air purification systems typically contain elements to replenish oxygen and remove carbon dioxide, carbon monoxide, trace organic contaminants, and particles. These systems are designed to handle normal loads on the spacecraft air, with adequate overdesign margins. However, they are not designed to deal with accidental large releases of contaminants into the atmosphere. Strategies such as coupling the odor/bacteria filter to a hand-held vacuum or turning the condensing heat exchanger to full cool have been devised to decontaminate the Shuttle in the event of a serious contamination problem. The last-resort solution is to depressurize the contaminated module and repressurize it with clean air as was done during Skylab.

### **Monitoring Airborne Contaminants**

Until recently, methods that met the severe weight and power constraints of space flight were not available to measure volatile contaminants on board spacecraft. Traditionally, contaminants had been trapped in evacuated steel cylinders or on adsorbent resins for identification and quantitation by GC/MS after the mission. Clearly, this approach is not useful during a mission. Because of concerns over thermodegradation of electronic devices, a combustion-products analyzer has been flown aboard the Shuttle since 1990. The device, which weighs approximately 1 kg, uses electrochemical sensors to measure selected toxic products of combustion. For high-risk EVA missions, a hydrazines monitor has been available in the air lock since 1991 to monitor selected propellants at ppb levels using ion mobility spectrometry (IMS). Instruments under development for Space Station Freedom include an IMS for rapid, nonspecific detection of volatile hydrocarbons and a GC/IMS device for periodic monitoring of 20 to 30 targeted chemicals that are often detected in spacecraft air. For the first time, short-term limits for contaminant exposure will be needed to interpret the monitoring results.

### **Setting Airborne Exposure Limits**

New SMACs were needed to provide monitoring goals for on board instruments, to deal with accidents where crew exposures last several hours, and to set limits for long-term exposures expected on the Station. The existing 7-day SMACs had been set many years ago without detailed documentation. Much has been learned recently about setting chemical exposure limits and more is known about the adverse effects of space flight on humans. The approaches described below have been developed in cooperation with the National Research Council Committee on Toxicology.

## **METHODS USED TO SET SPACECRAFT CONTAMINANT LIMITS**

### **Goals of Short and Long-Term Limits**

Setting specific limits in any situation requires that goals of the limits be clearly delineated. Short-term SMACs (1 and 24 h) are set for rare, accidental releases of chemicals into the air. Mild transient effects that do not limit a crewmember's performance are allowed. For example, mild headaches or eye irritation are acceptable; mild visual impairment would not be allowed. Long-term limits are set to protect the crew from any adverse effect to a reasonable level of risk. For example, the acceptable level of risk for a carcinogen was taken as the lower 95% confidence limit of a concentration that would impart a 0.01% excess risk of getting cancer as calculated using the linearized multistage model. In setting limits, the goal was to rely on high quality data, preferably from human exposure studies; however, animal data, noninhalation data, and structure-activity analyses often must be used to derive defensible values.

The guidelines described below should be viewed as a template for setting exposure limits. Databases for each chemical differ and it is often possible to argue scientifically from a database that certain factors or methods are not appropriate. The guideline is meant to be used when the database on a chemical is limited and no logical basis exists for selecting alternate factors or approaches.

### **Threshold-Type Effects vs. Cumulative-Type Effects**

Once original references have been obtained via a thorough literature search, each toxic effect induced by a chemical is reviewed and an acceptable concentration (AC) set for that specific effect and time of exposure. If an effect does not occur below some threshold concentration (e.g., central nervous system depression), then the ACs for that effect may be independent of time of exposure. On the other hand, many effects (e.g., liver damage) become more severe with prolonged exposure, so the AC will decrease with increasing exposure time. Because chemicals can induce both threshold and cumulative effects, the distinction between the two becomes uncertain. For example, a chemical may cause a cumulative effect at high concentrations, but below some threshold concentration an adverse effect is not induced no matter how long the exposure.

### **Application of Human Data**

Human data come from controlled exposures in a clinical environment, accidental industrial exposures, and long-term relatively low concentration exposures. Typically, the former are useful for setting short-term SMACs if the endpoints measured were relevant and there were 4 or more test subjects. Such studies are used to derive a no observed adverse effect level (NOAEL); because only a sample (n) of the population has been tested, the NOAEL is divided by  $\sqrt{n}/10$ . For effects that are tolerated for short times (e.g., headache) a semiquantitative dose response curve may be useful for estimating the mild-effect level. Accidental exposures and epidemiology data are seldom used because exposure concentrations often are unknown, endpoints are not carefully observed, or confounding factors obscure relationships between variables. Epidemiology data can be used to check predictions made from other data.

### **Estimates from Animal Inhalation Data**

Animal data must be reviewed with several reservations in mind. The first questions are whether the effects observed are adverse (or adaptive), and whether the animal model is appropriate to humans. For example, the hydrocarbon nephropathy induced in male rats seems to be irrelevant to humans, and hence should not be used for human risk assessment<sup>5</sup>. A change in organ weight in the absence of histopathological changes is considered adaptive. Adverse effects that do not follow a plausible dose-response relationship should be viewed with suspicion. Finally, some endpoints (e.g., narcosis) are gross indicators of serious effects and should be used with caution when predicting a NOAEL in humans. Usually, a NOAEL is estimated from animal data; however, under some conditions (when a dose response curve is well established), the "bench mark" approach has proven useful<sup>6</sup>.

The factor typically used in extrapolating an animal NOAEL to a human NOAEL is ten. The extrapolation is intended to account for "worst case" differences in metabolism and target tissue susceptibility between the model and humans. The extrapolation is done from the most sensitive species, although nonhuman primates can be more suitable models than a sensitive rodent species. However, if metabolic data show that the species-extrapolation factor should be less than ten, a smaller number is used in the estimate.

### **Noninhalation Data**

Inhalation data often are not available for a specific chemical. If toxicity data are available from other routes of administration, then they are used; when no toxicity data are available, structure-activity analysis is used. For noninhalation data, assumptions are necessary to relate the comparative absorptions of the chemical via inhalation and via the available route. Caution must be exercised if the chemical could induce local effects on the lung rather than systemic effects that would be evident from the noninhalation data. When no toxicity data are available on the specific chemical, structurally related chemicals are reviewed. Uncertainty factors applied to this analysis are based on the structural similarity of the chemicals involved, the consistency of the toxic properties of the chemicals, and the number of chemicals for which data are available.

### **Space-flight Induced Changes**

Some of the physiological changes that occur during space flight could leave astronauts more susceptible to certain toxicants. A safety factor of five has been determined for cardiac arrhythmogenic chemicals, and a factor of three for hematotoxicants and immunotoxicants. Cardiac arrhythmias are not common during space flight, but because of their potential seriousness, a relatively large factor was selected. After a few days in space, an astronaut's red cell mass decreases by approximately 10%; certain immune functions appear to decrease as well. Hence, a factor of three has been applied to hematotoxicants and immunotoxicants to estimate safe ACs for astronauts.

## **RESULTS FOR SELECTED CHEMICALS**

### **Indole**

Indole has never been detected in spacecraft air because of analytical limitations; however, it is undoubtedly present from metabolic sources. Short exposures cause nausea (human data) and prolonged exposures cause hematological effects and possibly leukemia (animal data). The new short-term SMACs were based on avoiding significant nausea and the longer-term SMACs were based on avoiding hematological effects which had been observed in mice, rats and monkeys exposed continuously for 90 days. A lower limit of 0.05 ppm on the long-term SMACs was set because this exposure would increase the normal load of indole from the gut by only 5% and indole causes only systemic toxicity (i.e., inhaled indole would not cause selective lung damage). The leukemogenic effects of indole were demonstrated by injection only and the data were not considered sufficient to develop a human risk estimate by the inhalation route.

### **Freon 113 (1,1,2-trichloro-1,2,2-trifluoroethane)**

Freon 113 is commonly used to clean electronic hardware before launch and is invariably found in samples of spacecraft air. Like most Freons it is not regarded as very toxic; however, experiments with dogs have demonstrated that Freon 113 can cause cardiac sensitization to arrhythmogenic chemicals. Applying a species extrapolation factor of 10 and a space flight factor of 5 to the 2500 ppm NOAEL observed in dogs gave a SMAC of 50 ppm. This was considered a threshold-type effect; therefore, the value was applied to all exposure times.

### **Octamethyltrisiloxane (OMTS)**

Siloxanes are common offgas products found in spacecraft air samples. A thorough literature search revealed no toxicity data for OMTS; however, data were available on hexamethyldisiloxane (HMDS) and dodecamethylpentasiloxane (DMPS). Comparison of HMDS and DMPS data by routes other than inhalation showed that HMDS was the more toxic. An inhalation study of HMDS in rats and guinea pigs showed that 4400 ppm (15 to 20

7 h exposures) caused no more than 10% decreases in liver and kidney weights without histopathological changes. The 4400 ppm NOAEL in rodents, after exposure time and species extrapolation adjustment, was used to calculate a NOAEL for HMDS. This NOAEL was reduced by a structure-activity factor of 3 to estimate a NOAEL for OMTS, the compound in question. The magnitude of this factor was judged from the fact that data were available on chemicals that structurally "bracketed" OMTS, but inhalation data were not available for one of them.

## CONCLUSIONS

Setting safe contaminant limits is an integral part of the strategy used to manage spacecraft air quality. A consistent framework has been established to interpret human and animal toxicity studies and to derive exposure limits ranging from 1 hour to 180 days. Where appropriate, the potential for increased susceptibility from space-flight-induced physiological changes has been incorporated into the analysis. Structure-activity analysis has been used when no specific toxicity data are available on the chemical of interest.

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## AIR QUALITY MONITORING IN SPACECRAFT: PRESENT AND FUTURE

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### ABSTRACT

The quality of the internal atmosphere of the Space Shuttles is maintained by removal of carbon dioxide, carbon monoxide, and some volatile organic compounds (the latter for odor control), and the replenishment of oxygen and nitrogen as necessary from storage tanks. The National Aeronautics and Space Administration (NASA) has long recognized the importance of monitoring spacecraft atmospheres to protect crew health and safety in these partially closed systems. Until recently, archived samples collected during flight and returned to Earth for subsequent analysis had been the only means of determining the quality of the Shuttle's atmosphere. Two real-time monitors have been developed within the past three years for use on the Shuttle, and two additional instruments are being built for Space Station Freedom (SSF).

This paper will present the methods used by the Toxicology Laboratory at Johnson Space Center (JSC) to collect and analyze samples from Shuttle atmospheres. Observed trends in constituents from samples of this "confined" atmosphere will be presented using data from recent missions. Finally, the "real-time" monitoring instruments currently used on Shuttle and those being built to monitor the SSF atmosphere will be described as well.

### INTRODUCTION

The partially closed-loop nature of spacecraft environments dictates the need for assessing and monitoring the air quality of the internal atmosphere. Toward this end, the National Aeronautics and Space Administration's (NASA) Toxicology Laboratory at Johnson Space Center (JSC) has been investigating and developing techniques to sample, analyze, and monitor the contaminants in spacecraft atmospheres. Sources of contamination in spacecraft can include: nonmetal material, human metabolism, hygiene products, food, utility and payload chemicals, fire extinguishant and clothing. The spacecraft's environmental control and life support system (ECLSS) is designed to maintain acceptable air quality in the spacecraft by removing carbon dioxide, carbon monoxide, trace volatile organics, and excess heat and moisture.

Until recently, in addition to temperature and humidity, only oxygen and carbon dioxide concentrations were routinely monitored in real time during Shuttle missions. However, air samples of the crew cabin are collected on all Shuttle missions and returned to the Earth for analysis by the JSC Toxicology Laboratory. Concentrations of methane, carbon monoxide, hydrogen and trace volatile organic compounds are determined from these archived samples. Additionally, most of the volatile organic compounds are positively identified by gas chromatography/mass spectrometry (GC/MS). Instantaneous "grab" samples are collected in evacuated cylinders near the end of each Shuttle mission; during selected missions (i.e. spacelabs, refurbished Shuttles) daily 24-hour integrated samples are collected on a sorbent resin.

Temporary degradations in air quality have occurred aboard the Space Shuttle<sup>1,2</sup> and must be anticipated during any long-duration space flight. Although archival sampling provides postflight information on the severity of the incidents, the goal of the JSC Toxicology Laboratory is to develop on-board monitors that can detect such events early, in "real time", and be available to measure the effectiveness of air decontamination efforts. The major obstacles to the development of real-time air monitors for Shuttle are the stringent requirements placed upon flight hardware. An air monitor for Shuttle must be compact, lightweight, microgravity-compatible, impervious to the vibration and shock of launch, and require minimal Shuttle resources such as power and crew time.

A prototype combustion products analyzer (CPA), the first real-time monitoring instrument developed by the JSC Toxicology Laboratory, has flown on each Shuttle mission since October 1990. This instrument was developed in response to minor thermodegradation incidents<sup>3,4</sup> that had occurred during Shuttle missions. A second real-time monitor was constructed to detect the presence of hydrazines in the airlock following extravehicular activities (EVA) since there is a risk of contaminating the airlock with these toxic propellants.

Consideration of monitoring requirements for longer missions, with an increased risk of chemical accidents, has led to the development of a prototype total hydrocarbon analyzer (THA) and a volatile organic analyzer (VOA) for Space Station Freedom (SSF). Both instruments use the emerging technology of ion mobility spectrometry.

## ARCHIVAL SAMPLES

### Collection

**Grab Samples.** Volume and weight restrictions dictate the size of the stainless steel cylinders (350 cc). Before they are stowed for flight, the cylinders are evacuated and certified clean by back-filling the cylinder with pure helium and running a GC/MS blank. The cylinder is then evacuated to at least  $10^{-5}$  torr before being sent to Kennedy Space Center (KSC) for stowage on board the spacecraft.

A prelaunch air sample is obtained just before the launch of each Shuttle, and at least two air-sample cylinders are flown on each mission. One cylinder is used to collect a sample of the Shuttle's internal atmosphere on the last day of the mission. The second cylinder is used if the crew detects an unusual odor or experiences symptoms (e.g. eye irritation) that may be related to degradation of Shuttle air quality. During Spacelab missions, 3 or 4 extra cylinders are stowed to collect samples of laboratory air when the crew first enters the spacelab module, and again during the early, middle, and late phases of the mission. The inflight air sample cylinders are transferred to JSC for analysis immediately upon the conclusion of the mission.

**Integrated Samples.** In addition to the air-sample cylinders described above an integrated sample is collected daily on the first flight of new or refurbished spacecraft and on all spacelab missions. The solid sorbent air sampler (SSAS) obtains integrated samples by pulsed sampling into a tube containing a solid sorbent. The SSAS consists of 8 tubes (5 in. x 1/4 in.) joined to an 18-port valve. Tube 8, the designated "transport position", is open to the atmosphere during all non-sampling times; therefore, it is not available as a sample collection tube. Each tube contains approximately 400 mg of Tenax™ GC. Prior to flight, each SSAS tube is cleaned by heating it to 250°C while helium is flowed over the sorbent. The cleanliness of all tubes is verified by GC/MS analyses before the SSAS is sent to KSC for stowage on the Shuttle. The verification procedure involves flowing helium over the heated tube (200°C) and collecting the volatile organics that are removed by a liquid nitrogen (LN<sub>2</sub>) cryotrap before transfer to the GC column.

During flight use, an air pump with a variable duty cycle permits air samples of a specified size to be pulled over the SSAS tube during a 24-hour period. Typical flow rates allow 1.0 to 1.5 liters of Shuttle air to be collected per sampling tube. At the conclusion of the 24-hour sampling period, a rotary selection valve permits the crewmember to switch to the next tube to collect another 24-hour integrated sample. This procedure is repeated each day of the mission until the last flight day, when the rotary selection valve is moved to the tube "8" position, where it remains until analyses are performed in the JSC Toxicology Laboratory. A unique feature of the SSAS is that tube contamination is minimized since the tube is never exposed to the ambient environment except during sampling.

### Analysis

**Grab Samples.** Air-sample cylinders are generally returned to the JSC Toxicology Laboratory within one or two days of landing. Sample cylinders stored aboard spacelabs are slower to return, and weeks may elapse before analyses can begin. Each cylinder is analyzed immediately by GC (Varian 3700) and GC/MS (HP 5890 GC and HP 5970 mass selective detector (MSD)). Samples are pulled through a gas sampling valve into a GC sample loop by a vacuum pump. Differential pressures are used to determine GC sample size. A Valco helium ionization detector (HID) is used to ascertain the concentrations of carbon monoxide and methane. A second GC (Varian) with a thermal conductivity detector (TCD) determines the hydrogen concentration in the sample. Screening runs on GCs with flame ionization and electron capture detectors are used to determine the GC/MS sample size.

For GC/MS analysis of organic vapors, the sample cylinder is heated to 50°C for 30 minutes before a sample volume (determined by the GC runs) is extracted into a (LN<sub>2</sub>) cryotrap. A 50 m x 0.25mm (i.d.) capillary column with a 1 μm film of carbowax is used to separate the multicomponent samples. The GC column is held at an initial temperature of 35°C for 10 minutes, then the GC oven is ramped to 175°C at 2°C/min. The MSD detects ions over a 25-350 dalton mass range; the lower limit permitting the identification and detection of methanol and acetaldehyde.

**Integrated Samples.** Integrated SSAS samples are analyzed with the same GC/MS method described above. Each SSAS tube is individually heated to 200°C upstream from the LN<sub>2</sub> cryotrap. Helium gas flowing at approximately 10 cc/min is allowed to sweep the sample out of the heated tube and into the cryotrap. The cryotrap is then heated to transfer the volatile organics compounds to the GC. The GC/MS conditions are identical to those

used for the sample cylinders. A volume correction factor is applied to the final calculated concentrations of some compounds to account for their relatively low retention volumes in Tenax™ GC.

### Mission Results

Typically isopropanol, which used as a cleaning agent before launch, is the only compound found in preflight samples; this result is testimony to the effectiveness of the prelaunch purge system used to remove the offgassed organic vapors from the cabin. Results obtained from analyses of samples from the STS-26 through STS-52 missions are shown in Table 1. The many compounds detected (typically >80 each SSAS tube) are grouped into chemical classes for clarity. Each class is divided further into the total number of times a member of a compound class (can be more than one per mission) was seen at a concentration above or below 1 mg/m<sup>3</sup> from STS 26 through STS 52. With few exceptions, compounds in concentrations above 1 mg/m<sup>3</sup> are the focus of the toxicological assessments of Shuttle air quality. The concentrations (C) obtained on "n" contaminants from each flight are used to estimate the aggregate toxicity (T value) of the air by comparison to the respective spacecraft maximum allowable concentrations (SMAC) as follows:

$$T = C_1/SMAC_1 + C_2/SMAC_2 + C_n/SMAC_n$$

These mission analyses have never shown an unacceptable aggregate-contaminant concentration (T > 1) in the Shuttle atmosphere.

Methane and hydrogen (Table 2) serve as qualitative internal standards because the concentrations of these metabolic byproducts continuously increase during the mission since they are not removed efficiently by the ECLSS. If these compounds are found in unusually low concentrations or are totally absent from the sample, this suggests a sample-collection problem (i.e., valve leak). The data in Table 1 show that the contaminant classes of alcohols, ketones, and halocarbons are present in the highest concentrations in the nominal Shuttle atmosphere. The alcohols emanate from medical and hygiene supplies and the ketones from crew metabolism. Halocarbon sources include the fire extinguishant and offgassing of residual compounds from manufacturing or component cleaning processes.

### REAL TIME AIR-QUALITY MONITORS

Archival samples unquestionably provide valuable information on Shuttle air quality; however the absence of real-time data and the inability to detect some compounds such as formaldehyde, hydrazines, and inorganic acids has led to the development of real-time Shuttle air quality monitors. There have been five minor thermodegradation incidents during Shuttle flights. Although the crew did not experience any permanent adverse health effects, these incidents clearly demonstrate the potential for significant air-quality degradation. The combustion products analyzer (CPA) was developed in response to the early thermodegradation incidents that occurred aboard Shuttle. A hydrazine monitor was required to detect the presence of hydrazines in the airlock after an EVA.

### Combustion Products Analyzer

The JSC Toxicology Laboratory and Exidyne Instrumentation Technology (EIT) have developed a prototype CPA<sup>5</sup> that can alert the crew to incipient thermodegradation events and provide data to determine the effectiveness of decontamination efforts that follow such an event. The primary function of the Shuttle CPA is to determine when the Shuttle atmosphere is safe for the crew to breathe after a serious thermodegradation incident.

**Description and Methods.** The CPA (Figure 1) is a hand-held, battery powered instrument containing four electrochemical sensors that detect and quantify hydrogen fluoride (HF), hydrogen chloride (HCl), hydrogen cyanide (HCN) and carbon monoxide (CO). These four compounds have been deemed the most toxicologically significant in view of the Shuttle materials that are most prone to thermodegradation. The CPA has been exposed to combustion atmospheres<sup>4</sup> in ground-based testing to demonstrate its ability to track the concentrations of the four targeted compounds.

Each day of the mission, the crew destows the CPA, activates the unit, and records the concentration displayed for each target compound. The CO sensor exhibits a cross-sensitivity to hydrogen (approximately 10:1) that accumulates in the spacecraft atmosphere from human metabolic processes. Therefore, recorded CO baseline readings are used to normalize the CO sensor response in the event of thermodegradation. An improved CPA is being constructed that contains a hydrogen sensor and microprocessor that automatically compensates the CO sensor display for the hydrogen cross-sensitivity.

**Mission Results.** The CPA has flown on every mission since STS 41 (October 1990). Typical baseline values for the four sensors during the course of the missions are shown in Figure 2. The sensors have remained stable during the mission with the exception of the CO sensor, which is responding to hydrogen accumulations. A slight increase observed in the HF sensor baseline has not been associated with a contaminant in the Shuttle atmosphere.

## Hydrazine Monitor

**Description and Methods.** The hydrazine fuels used in the propulsion systems of satellites, the Shuttle, and the proposed SSF are toxic compounds; their SMACs are as low as 2 parts per billion (ppb). A crewmember returning from an EVA could contaminate the airlock if hydrazines from a leaking satellite or spacecraft engine were to adhere to the suit. A prototype hydrazines monitor, based on doped-chemistry ion mobility spectrometry, has been selected because of its sensitivity (<10 ppb) and adaptability to microgravity conditions.

**Mission Results.** Before flight on the Shuttle, the hydrazine monitor was tested<sup>6</sup> at the White Sands Test Facility (WSTF). The hydrazine monitor was exposed to known concentrations of hydrazines under conditions similar to those that would be encountered in the Shuttle. This testing clearly demonstrated the ability of the hydrazine monitor to unambiguously detect hydrazines if present in an atmosphere being monitored.

The hydrazine monitor has been used on two EVA Shuttle missions (STS 37 and STS 49) which posed an increased risk of hydrazines contamination. After the EVA crews returned to the airlock, the hydrazine monitor was used to ensure that hydrazine had not been inadvertently introduced into the airlock. The hydrazine monitor detected a very small quantity of ammonia (<1ppm) in the airlock at the conclusion of one EVA, but hydrazines were not detected following any EVA during these flights.

## THA and VOA

These two instruments form a comprehensive volatile organic compound monitoring strategy for spacecraft. The quick response of the THA makes this instrument well-suited to first alert functions. Although the instrument is not designed to positively identify volatile organic compounds, it will respond quickly if the total volatile organic concentration exceeds a preset threshold. The VOA requires 1-2 hours to complete an analysis; however the results of an analytical run include accurate identification and quantitation of volatile organic compounds in the atmosphere. When the THA detects degraded air quality onboard SSF, the VOA will provide the data (contaminant identity and quantity) necessary to enact appropriate decontamination procedures.

**THA Description.** A THA for spacecraft must possess a fast response time, near universal response to hydrocarbons (except methane), and the other previously mentioned characteristics of flight hardware. A THA breadboard was constructed based upon ion mobility spectrometry. In an ion mobility spectrometer, analyte molecules are ionized (unusually by a Ni<sup>63</sup> source), then ions of the same charge are pulsed into a "drift region" where the presence of a weak electrical field separates the ions based on size and shape. Mobility spectra are generated by measuring and recording the time required for an analyte ion to traverse the drift region. The magnitude of the signal is used to quantitate the analyte. Positive and negative ions are alternately pulsed into the drift region to generate the necessary data for comprehensive total hydrocarbon analysis.

An ion mobility spectrometry based THA will meet the criteria described above and it has additional important advantages. The THA will respond to compounds, i.e., freons, that are not normally detected by other THA devices. Most importantly, the THA, with appropriate algorithms (i.e., neural network), can correct for normal background contaminants such as acetone that are present in moderate concentrations. Moreover, the THA is a near universal detector but does not respond to nominal atmospheric contaminants such as carbon dioxide and methane.

**VOA Description.** The VOA is designed to accurately identify and quantify trace volatile organic compounds in spacecraft atmospheres. Gas chromatography/ion mobility spectrometry (GC/IMS) was selected over gas chromatography/mass spectrometry because of power, weight, and volume restrictions on spacecraft. However, with appropriate algorithms and custom libraries the quality of information derived from GC/IMS equals or exceeds that generated by GC/MS in the proposed operational scenarios. A breadboard VOA was configured with a specially designed concentrator and a mini-GC (MTI) interfaced directly into the ionization region of a heated IMS. The IMS is operated at 150°C to insure reproducible spectra and to keep the cell clean. Initial sensitivity and selectivity studies have been encouraging.

## CONCLUSIONS

Analytical results from archived samples taken on Shuttle missions verified that the crew cabin and spaccelabs have had acceptable air quality. This can be attributed to careful selection of materials and proper toxicological and containment assessment of the chemicals permitted aboard the Shuttle. However, concerns about contingency events and the compounds not representatively sampled by the current archival methods have led to the development of real-time instrumentation for the Shuttle. The CPA, composed of four electrochemical sensors targeted to specific compounds, can provide information on the quality of the air in an enclosed space after a thermodegradation event. The hydrazine monitor, based on ion mobility spectrometry, has been shown to detect hydrazines effectively at the reduced pressures used in the Shuttle airlock.

As a next step, the JSC Toxicology Laboratory has formulated a strategy for real-time air quality monitoring aboard spacecraft that uses the thorough analysis provided by the VOA to complement the first-alert protection

afforded by the CPA and THA. Breadboard VOA and THA are ion mobility spectrometry instruments have been constructed and are presently being evaluated. The IMS characteristics, sensitivity, compact size and minimum power requirements, are important advantages for spacecraft as well as field screening and indoor air monitoring applications. Ion mobility spectrometry is an emerging technology with great potential to serve both the environmental and space communities.

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**Table 1: Chemical Contaminants During Missions STS-26 through STS-52**

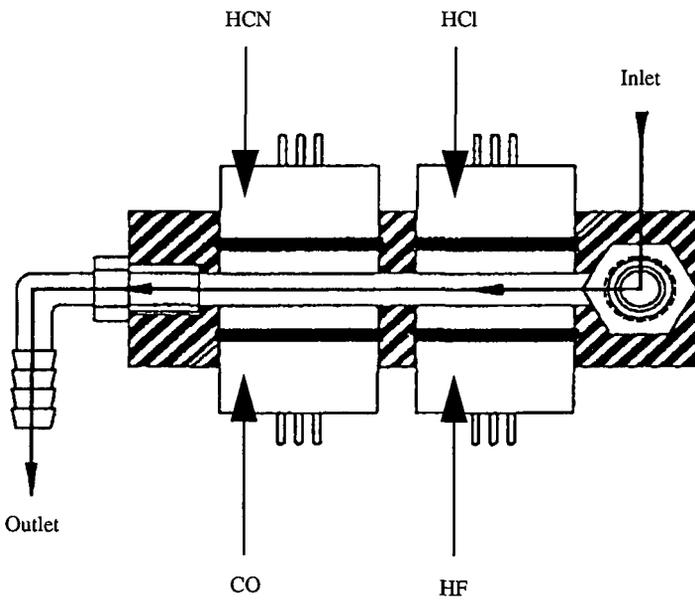
**AVERAGE CONCENTRATION RANGES**

Contaminants	Number of Missions (Concentration in $\text{mg}/\text{m}^3$ )	
	$<1 \text{ mg}/\text{m}^3$	$\geq 1 \text{ mg}/\text{m}^3$
Alkanes *	17	3
Alkenes	11	0
Alcohols	44	46
Ketones	56	14
Aromatic hydrocarbons	36	2
Esters	11	0
Aldehydes	19	0
Silicone compounds	32	6
Halocarbons	106	22
Miscellaneous	11	0
* Excluding methane		

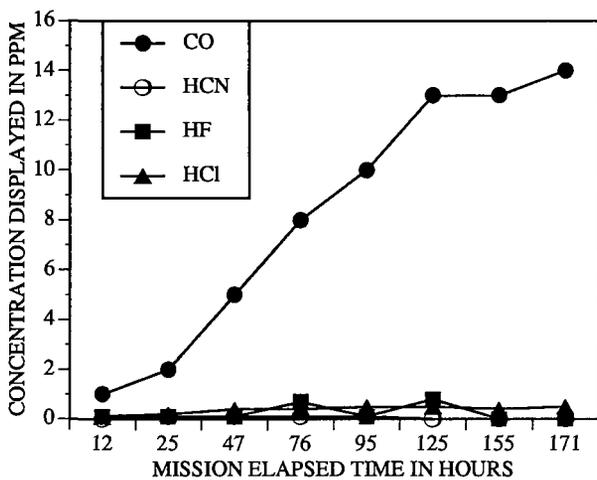
**Table 2: Hydrogen and Methane Contaminants During Missions STS-26 Through STS-52**

**AVERAGE CONCENTRATION**

<b>Hydrogen</b>	<b>Methane</b>
<b>8.3 mg/m<sup>3</sup></b>	<b>46 mg/m<sup>3</sup></b>



**Figure 1: CPA Sensor Block**



**FIGURE 2. Concentrations Displayed by the CPA During the STS-56 Mission (April 1993).**

### *Shuttle Solutions*

*There's a gripe about odors in space  
In this era, when astronauts race  
    Exercising with strain  
    So their muscles sustain  
All their tone, in that weightless small place.*

*This short mission will take but one week  
Physiological tests: at their peak  
    With great physical toil  
    Tons of sweat, a true spoil  
This experiment's really quite sleek!*

*Please remember...our windows are shut  
And the doors are well sealed, in this hut  
    Seven people, here live  
    All our faults, we forgive  
We're a team! There's no room for one nut!*

*There are problems with odors...come...look  
Meet the captain, the crew and the cook  
    A solution I'll pave  
    To the problem you gave...  
It would help...If a shower you took!*

*Hector Javier Leño  
Toxicology Laboratory  
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## **SUBMARINE AIR QUALITY: RELATIONSHIP TO HUMAN BODY BURDEN**

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### **ABSTRACT**

A preliminary survey of the distribution of the volatile organic components (VOCs) present in submarine air was performed at various stages of an 82 day patrol. Expired air from one of the crew members was also surveyed during the patrol. Because the chemical composition of the samples obtained was extremely complex, the data were presented as the total GC/MS ion count for each of 10 chemical classes. In the air samples, 249 components were identified; in the breath samples, 241. The relationship of the air composition to the breath samples (body burden) is presented.

### **INTRODUCTION**

The submarine represents a unique environment in which individuals may be confined for periods of up to 90 days. Thus, any VOC emissions arising from sources as the off-gassing of equipment components, smoking, cooking, combustion products of fires, and medical supplies must be controlled. Review articles<sup>1,2</sup> summarizes previously published information on VOCs in submarine air; other articles<sup>3,4</sup> focus on atmospheric monitors that ensure air quality. The work presented here is an extension of a preliminary study<sup>5</sup> directed toward characterizing, in detail, submarine air and assessing the human body burden resulting from exposure to this environment.

### **EXPERIMENTAL**

The experiments described were conducted at selected intervals during, and upon completion of, an 82 day patrol. One crew member, a non-smoker, provided samples of the expired breath before, during, and after patrol. All collections were made while he was in a fasting, resting condition. The pre-patrol sample (baseline) was collected before exposure to the submarine atmosphere and the post-patrol sample was collected in a field laboratory adjacent to the submarine.

Air samples were collected by drawing 20 l of compartment air at a rate of 300 cc/min through glass cartridges, ¼ inch O.D. and 7 inch long, packed with 600 mg of 60/80 mesh Tenax GC. Upon completion of the sampling period, the cartridges were capped with Teflon plugs, placed in a protective container, and refrigerated.

Breath samples were collected by having the subject inhale zero grade air, purified by a cooled (0°C) charcoal trap and particle filter, and exhaling into a 40 l Teflon bag. The subject inhaled through a two-way Rudolph valve and exhaled through a Teflon transfer line. The contents of the 40 l Teflon bag was samples by pumping 20 l of the exhaled air through the glass cartridge in the same manner.

The collected samples were preconcentrated by transferring the contents of the first Tenax GC cartridge to a second Tenax GC cartridge. This minimized the quantity of water vapor collected on the first cartridge. The contents of the second cartridge, dosed with an internal standard, was then inserted into a desorption oven attached to a computer assisted gas chromatograph/mass spectroscopy (GC/MS/COMP) system. Desorption was accomplished by heating the cartridge (250°C) in an inert gas stream and collecting the volatiles in a cryogenically cooled trap. The trap was then rapidly heated and the contents flushed onto a high resolution GC column with the helium carrier gas temporarily by-passed through the cartridge. The sample on the high resolution GC column was analyzed in a cyclic scan mode on a MAT 311A mass spectrometer using the Spectro 200 data system (Figure 1). A spectrum-enhancement algorithm was used to produce a spectrum free of background and contaminating components. The peak areas obtained were compared to the area of the internal standard and subjected to a retention-time normalization procedures before an historical library search routine was performed.

## RESULTS

The results presented in Table 1 identify the distribution of VOCs in selected submarine air samples collected at various stages of patrol. Because the number of components found was large, the data were reduced to reflect the total quantities of material in each of 10 major chemical classes<sup>9</sup>. The values presented represent the total ion count of all components comprising each class. The last column identifies the number of MS detector saturated peaks found in each class. To intercompare samples, these peaks were arbitrarily assigned a value of  $2 \times 10^6$  since it is not possible to give accurate ion count values for such detector saturated peaks. This assignment permits comparisons even though the degree of variation of the air samples (Table 1) compared to the breath samples (Table 2) is biased by the larger number of MS saturated peaks in the submarine air samples. Therefore, the total ion counts for the submarine sample(s) are very conservative in comparison to the breath samples.

Table 2 presents the distribution of the various chemical classes of VOCs found in the baseline breath sample, and in the breath samples collected during and after patrol. A summary of the total number of components and MS saturated peaks occurring in each sample set, is presented.

It is clear from the data that the VOC concentrations in the submarine air (Table 1) are ~ 10 fold larger than the post-patrol expired breath values; and ~ 20 fold greater than they are in the pre-patrol breath sample. The major classes of VOCs in submarine air were the alkanes, aromatics, and oxygen-containing organic components. The major classes in the baseline breath sample were the alkenes and the oxygenated organic components. Of the 18 components present in the alkene class, isoprene represented the major component. In the submarine sample, methyldecene-2 was the major component in the alkene class and was the only MS saturated component of the six components comprising this class. At the start of the patrol, the total VOC levels in submarine air were ~ 13 fold larger than the levels

**Table 1. Distribution of chemical classes in submarine air samples**

Compound Name	Submarine Air <sup>A,B</sup> Total Ion Counts 10 <sup>3</sup>			Total No. of Components Per Class	No. of MS Detector Saturated Peaks
	Pre-Patrol	Patrol	Post-Patrol		
Alkanes	54,454	73,877	6,8521	68	35
Alkenes	3,105	8,422	3,118	6	1
Cycloalkanes	5,350	10,757	8,361	18	5
Aromatics	14,968	20,314	28,236	62	13
Oxygenated cycloalkanes	2,196	2,153	2,267	13	1
Oxygenated aromatics	518	1,975	548	20	0
Oxygen containing	18,203	30,756	24,186	35	10
Halogen containing	6,142	14,467	8,047	10	3
Nitrogen containing	6,490	10,165	12,130	14	6
Sulfur containing	6,000	6,000	6,000	3	3
	117,426	178,886	161,414	249	77

<sup>A</sup>Total ion counts based on mass spectrum response for 20 l air sample and corrected for background  $\times 10^3$ .

<sup>B</sup>Component peaks that saturated MS detector response arbitrarily given total ion count of  $2000 \times 10^3$ .

**Table 2. Distribution of chemical classes in human breath samples**

Compound Name	Breath Air <sup>A,B</sup> Total Ion Counts 10 <sup>3</sup>			Total No. of Components Per Class	No. of MS Detector Saturated Peaks
	Pre-Patrol	Patrol	Post-Patrol		
Alkanes	847	29,387	8,250	56	9
Alkenes	3,404	2,052	1,346	5	0
Cycloalkanes	402	4,225	284	16	2
Aromatics	487	4,402	680	47	1
Oxygenated cycloalkanes	155	74	48	12	0
Oxygenated aromatics	606	361	435	15	0
Oxygen containing	2,240	9,125	1,397	53	2
Halogen containing	299	6,688	2,196	13	1
Nitrogen containing	170	2,064	99	16	1
Sulfur containing	390	2,032	86	8	1
	9,000	60,410	14,821	241	17

<sup>A</sup>Total ion counts based on mass spectrum response for 20 l air sample and corrected for background  $\times 10^3$ .

<sup>B</sup>Component peaks that saturated MS detector response arbitrarily given total ion count of  $2000 \times 10^3$ .

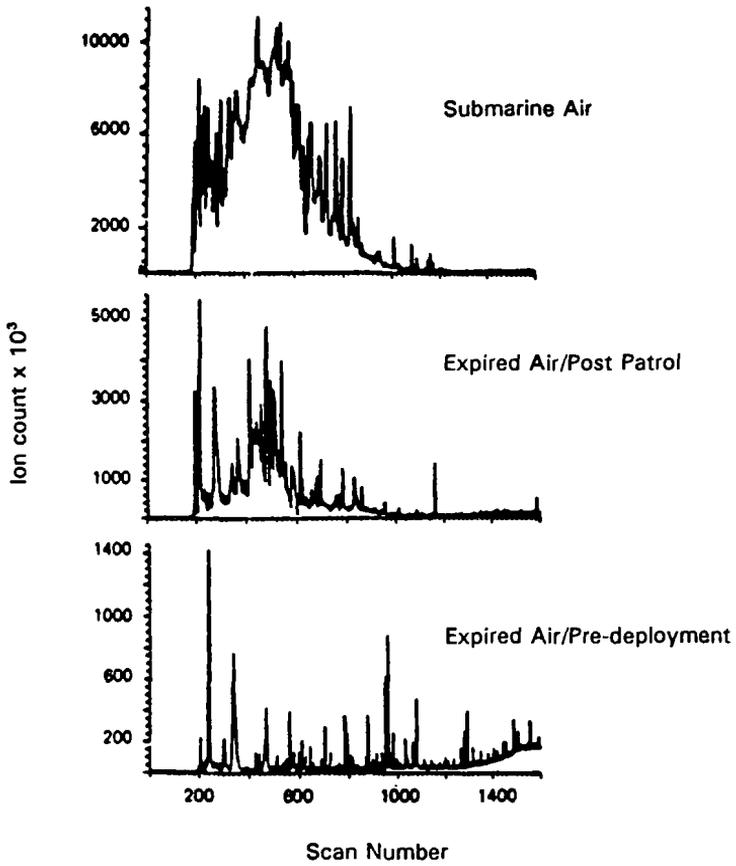


Figure 1. Typical total ion chromatograms of selected air and breath samples.

in the breath sample; following patrol were ~9 fold larger. The breath sample collected during patrol were higher in sulfur- and halogen-containing components than either the pre-patrol or post-patrol breath samples.

It is of interest to note that the breath sample from the non-smoking crew member yielded a benzene baseline ion count of 39, a patrol value of 84, and a post-patrol value of 36, while the submarine pre-patrol air sample yielded a value of 43. However, both the patrol and post-patrol submarine air samples yielded saturated ion counts for benzene. Toluene exhibited saturated ion counts for all three sample types (pre, patrol- and post-) collected from the submarine air and represented the only component in the aromatic class to exhibit a saturated peak in the patrol breath sample. Why the benzene value was so low in the patrol breath sample as opposed to toluene is unclear, particularly since smoking is permitted on-board on a limited basis. However, the patrol breath sample was collected following a snorkling exercise.

It is also of interest to mention that in the oxygen containing compound class, 6-methyl-5-heptene-2-one and 6,10-dimethyl-5,9-undecadiene-2-one were identified in both the pre- and post-patrol breath samples, but not in the patrol sample. These two compounds were reported in the breath samples of both normal and diseased subjects, as well as in the baboon<sup>7</sup>. Their presence has been proposed as representing products of a possible shunt pathway in the mevalonic acid pathway. Their absence in the patrol breath sample might be attributed to the four-fold increase in the total quantities of other oxygenated compounds present in this sample.

## DISCUSSION

The overall composition of submarine air, like all indoor air environments, is a reflection of various emission sources. The complexity of the chemical species comprising submarine air is not surprising since many of the emission sources in the submarine also appear in the workplace and home. However, the total quantities of such components in submarine air, as would be expected in a closed system, are substantially higher than found in typical indoor/outdoor relationships<sup>8</sup>. Therefore, the main emphasis when monitoring submarine environments should be on the potentially more health related components present, and on ensuring that their presence is minimized by means of suitable air exchange rates or efficient environmental control systems. Occupational exposure to the submarine environment changed the distribution of the total ion counts across virtually all classes of compounds in the expired breath. For example, alkenes were predominantly desorbed from the subject before patrol; but after patrol, the distribution of expired VOCs shifted to alkanes and halogenated substances. This suggests that the body tissues has a greater propensity to absorb and retain alkanes and halogenated organics than the other classes of VOCs or, that the other classes of VOCs are more easily metabolized and/or eliminated. Concerns about the body burden and pulmonary clearance of these compounds, their biotransformation products, and considerations relating to possible metabolic, physiological, or toxicological significance must await a more comprehensive study.

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## CABIN AIR QUALITY ABOARD COMMERCIAL AIRLINERS

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### ABSTRACT

The purpose of the study, conducted for the U.S. Department of Transportation, was to develop information to be used for determining health risks from exposure to environmental tobacco smoke (ETS) and other pollutants for airliner occupants. ETS contaminants (nicotine, respirable suspended particles, and carbon monoxide) as well as ozone, microbial aerosols, carbon dioxide and other environmental variables were measured on 92 randomly selected flights, including 69 smoking and 23 nonsmoking flights.

Respirable suspended particles averaged  $175 \mu\text{g}/\text{m}^3$  in coach smoking sections compared to background levels of 35 to  $40 \mu\text{g}/\text{m}^3$  on nonsmoking flights. Nicotine levels were  $13.4 \mu\text{g}/\text{m}^3$  in smoking and below  $0.3 \mu\text{g}/\text{m}^3$  in nonsmoking sections and on nonsmoking flights. Measured carbon dioxide levels averaged 1500 ppm, well above the American Society of Heating, Refrigerating and Air Conditioning Engineers' comfort criterion of 1000 ppm. Levels of carbon monoxide, ozone and microbial aerosols generally were quite low.

## INTRODUCTION

The airliner cabin environment has been of great concern for the last twenty years to various elements of the U.S. Federal Government, special interest groups organized to advocate public or industry positions, and the general public itself. Passenger complaints about smoking led to segregating smoking passengers in the early 1970s. Later concerns about stratospheric ozone prompted standards (0.25 ppm maximum instantaneous level and 0.1 ppm as time-weighted three-hour standard) for the ozone concentration in airliner cabins<sup>1</sup>. Public Law 100-200, enacted in 1987 and effective for two years beginning in April 1988, prohibited smoking by passengers on any scheduled domestic commercial flight of two hours or shorter duration. At the same time, the U.S. Department of Transportation (DOT) received Congressional approval to conduct a study to resolve certain technical questions related to potential continuation or broadening of the prohibitions in the law.

The purpose of the study<sup>2</sup> was to develop information to be used for determining health risks from exposures to ETS for nonsmoking airliner occupants as well as risks from other pollutants of concern for all airliner occupants. Although prior studies<sup>3,4</sup> were useful in suggesting ranges of concentrations of ETS tracers encountered in the general airliner cabin environment, the monitored flights were not randomly selected and the number of observations was generally small, precluding any generalization of the results. Similarly, determining factors (e.g., smoking rates, ventilation systems, seating patterns) of ETS concentrations for the general airliner cabin environment were not investigated in depth.

## METHODS

### Selection of Flights

The target sample size for the study was 60 to 120 smoking flights on jet aircraft, including some international flights. A smaller set of 20 to 40 nonsmoking flights was targeted to provide a baseline for comparison. The target sample size for nonsmoking flights was smaller because flight-to-flight variations in ETS contaminant levels were expected to be lower than for smoking flights.

A total of 70 airports that collectively accounted for 90 percent of U.S. enplanements during 1987 was used as the sampling frame for selection of flights to be monitored. Airports of departure were randomly selected for study flights to provide proportional representation of airports associated with all smoking and nonsmoking flights scheduled for departure during January 1989, based on computer data files supplied by DOT. The random selections were made separately for smoking and nonsmoking flights. The specific flights to be monitored were chosen by randomly chaining together the selected airports of departure, subject to constraints relating to the smoking/nonsmoking status of flights.

### Measurements

Air pollutants were selected for monitoring that had known or suspected sources in the aircraft and could be monitored or sampled in airliner cabins with small, unobtrusive instrumentation. The ETS contaminants monitored during the study were nicotine, respirable suspended particles (RSP), and carbon monoxide (CO). The other pollutants that were monitored were ozone and microbial aerosols. In addition, carbon dioxide (CO<sub>2</sub>) was monitored. The monitoring package configured for the study consisted of instruments and sensors for measurement of time-varying concentrations of contaminants in addition to samplers for collection of time-integrated samples. It also included a data acquisition system for recording outputs from the continuous monitors. The instrument was packaged in a single, compact carry-on bag (approximately 18 inches long, 9 inches wide, and 9 inches high) typical of that carried by airline passengers.

Nicotine was measured through collection of time-integrated samples and CO was measured with portable continuous monitors (Table I); RSP was measured both by integrated and continuous methods, with an optical sensor in the latter case. CO<sub>2</sub> and ozone were measured with time-integrated samples whereas short-term samples were collected for microbial aerosols (bacteria and fungi) near the end of each flight, prior to descent. Temperature, relative humidity, and cabin air pressure were monitored continuously with portable sensors. Air exchange rates were measured using constant release and integrated sampling of perfluorocarbon tracers (PFTs). Smoking rates were estimated through technician observations of the number of lighted cigarettes during a one-minute interval every 15 minutes and collection of cigarette butts at the end of most monitored flights. All aspects of the measurement protocol were pretested on four commercial flights that were monitored over a three-day period in March 1989.

The 92 study flights were monitored over a 10-week period between April and June 1989. Monitoring was performed by each technician at an assigned seat. Based on pretest monitoring at a variety of locations, the following four locations were chosen for monitoring on smoking flights: coach smoking section; boundary region of the

no-smoking section within three nonsmoking rows near the coach smoking section; middle of the no-smoking section; and remote no-smoking section (i.e., as far as possible from coach smoking, usually near the first-class smoking and no-smoking sections). Because less substantial variations were expected on nonsmoking flights, two locations (middle and rear of the plane) were chosen for those flights. ETS contaminants were monitored at all seat locations and other pollutants were monitored at half of the locations. The instrument package typically was placed on the technician's lap or lap tray to obtain measurements of contaminants most representative of passenger breathing levels.

## RESULTS

### Temperature, Humidity, Pressure and Air Exchange

The average measured temperature on study flights was near 76 °F (range: 71 to 81 °F). Measured relative humidity levels were quite low, ranging from 5 to 38 percent across all flights, but were even lower for smoking (average of 15.5 percent) than nonsmoking flights (average 21.5 percent). The average cabin pressure was lower for smoking (635 mm Hg) than for nonsmoking (686 mm Hg) flights. Both the lower humidity and the lower pressure are consistent with higher altitudes that would generally be reached on the longer-duration smoking flights. For aircraft without recirculation, the pattern of measurement results indicated that there generally was insufficient mixing of PFTs throughout the airliner cabin for the results to be indicative of prevailing air exchange rates. In the case of aircraft with recirculation, the measured air exchange rates generally were consistent with but somewhat higher than nominal rates based on information provided by equipment manufacturers and airline operators.<sup>5</sup>

### Passengers, Smoking, and Concentrations of ETS Contaminants

The load factor (i.e., percent seating capacity filled by passengers) averaged 76 percent for smoking flights on narrow-body aircraft (average passenger capacity of 138) and 64 percent for smoking flights on wide-body aircraft (capacity 288). For the nonsmoking flights (capacity 135), the average load factor was 70 percent. On the average, there were 18 passengers in the coach smoking section (13.7 percent of all passengers). The average smoking rate per smoking-section passenger was 1.5 cigarettes per hour (range: 0.2 to 3.5 cigarettes per hour per passenger) during the period when smoking was allowed. An average of 68 cigarettes per flight was smoked by passengers in the coach smoking section on the monitored smoking flights.

Average values for various measurement parameters related to particle-phase and gas-phase ETS contaminants are summarized by monitoring location for both smoking and nonsmoking flights in Table II. RSP concentrations were highest in the smoking section, averaging near 175  $\mu\text{g}/\text{m}^3$ , and results for the gravimetric and optical methods were highly consistent. In other locations, however, the two methods yielded differing results. There was greater uncertainty for the gravimetric measurements due to relatively short monitoring durations for a number of flights. For example, 60 minutes of sampling duration (or about 80 minutes flight duration) on a nonsmoking flight would correspond to a sample volume near 0.1  $\text{m}^3$ . For this case, a laboratory uncertainty in mass determination of  $\pm 10 \mu\text{g}$  could result in measurement values ranging from -100 to + 100  $\mu\text{g}/\text{m}^3$  for a prevailing concentration near zero.

Cabin-wide optical results were more strongly correlated ( $r = 0.6$ ) with smoking rates than were the gravimetric results ( $r = 0.3$ ), and optical concentrations in the smoking section were also more strongly correlated ( $r = 0.6$ ) with nicotine concentrations than were the gravimetric concentrations ( $r = 0.5$ ). However, because the gravimetric method has a long history of successful use in various types of environments, neither type of measurement result can be ignored. The values obtained from averaging the results of the two methods (Table II) indicate that differences across the no-smoking sections of the aircraft for smoking flights and differences between these no-smoking sections and nonsmoking flights were less pronounced than differences involving the smoking section. The combined results for nonsmoking flights are consistent with RSP values that have been reported for other nonsmoking environments<sup>6</sup>. The one-minute peak RSP concentrations indicated some migration of ETS contaminants into the no-smoking sections on smoking flights.

Observed effects of tobacco smoking, based on gas-phase measurements, were more discernible for nicotine than for CO (Table II). Beyond the marked increase in nicotine in the smoking section, the boundary region of the no-smoking section was most affected. Differences between nicotine levels for the remaining no-smoking locations and levels on nonsmoking flights were within the range of measurement uncertainty, but nicotine levels were more often above detection limits in the no-smoking locations of smoking flights than on nonsmoking flights. The only discernible effect for CO was in the smoking section itself. CO levels generally were highest before aircraft were airborne, both for smoking and nonsmoking flights, due to intrusion of ground-level emissions.

Both nicotine and RSP concentrations in the coach smoking section were strongly related to observed smoking rates in that section<sup>7</sup>. This relationship also persisted in the boundary region near coach smoking, though not as strongly. For the other no-smoking sections, there was no apparent relationship between ETS levels and smoking rates. Within the boundary region, ETS concentrations generally were higher when the technician was seated within one or two rows of coach smoking than when the boundary seat was three or more rows away.

#### Concentrations of Other Pollutants

Monitored ozone levels were relatively low (Table III), averaging an order of magnitude below the three-hour standard of 0.1 ppm and never exceeding this level. Bacteria levels were higher than fungi levels and somewhat higher in smoking than nonsmoking sections, but the measured bacteria and fungi levels in all cases were low, relative to those that have been measured in residential environments through cross-sectional studies<sup>8</sup>.

Relatively high CO<sub>2</sub> levels were measured (Table III), averaging over 1,500 ppm across all monitored flights. Measured CO<sub>2</sub> concentrations exceeded 1,000 ppm, the American Society of Heating, Refrigerating and Air Conditioning Engineers (ASHRAE) level<sup>9</sup> associated with satisfaction of comfort (odor) criteria, on 87 percent of the monitored flights. Depending on assumed CO<sub>2</sub> exhalation rates, measured levels were as much as twice those predicted by a cabin air quality model. Even if the measured levels were to be lowered by half, however, CO<sub>2</sub> concentrations would still exceed 1,000 ppm on 24 percent of the study flights.

Average CO<sub>2</sub> levels measured in the middle of airliner cabins were examined in relation to the type of aircraft, load factor, air recirculation, and the nominal ventilation rate (expressed as cfm of fresh air per passenger)<sup>10</sup>. Narrow-body aircraft had higher CO<sub>2</sub> levels (1700 ppm) than wide-body aircraft (1200 ppm). The narrow-body aircraft have a smaller volume per passenger on the average, and the monitored flights were more fully occupied than the wide-body aircraft studied. Aircraft with recirculation had slightly higher CO<sub>2</sub> levels on the average than aircraft with 100 percent fresh air. Both the load factor and ventilation rate had very strong relationships with CO<sub>2</sub>; levels increased as the load factor increased and decreased as the ventilation rate increased. However, even for a subset of 12 flights with ventilation rates of 35 cfm per passenger or greater, the average CO<sub>2</sub> level (1,237 ppm) was above 1,000 ppm.

#### CONCLUSIONS

Levels of ETS contaminants monitored during the study were substantially higher in smoking sections of the aircraft than in nonsmoking areas, and these levels were strongly correlated with observed smoking rates. There was some evidence of ETS migration to the no-smoking boundary region near the smoking section, particularly for RSP concentrations in this region that were related to smoking rates and distance from the smoking section. Monitored CO<sub>2</sub> levels were sufficiently high and monitored humidity levels were sufficiently low to pose potential comfort problems for aircraft occupants. Ozone levels on all monitored flights were well within existing standards for airliner environments, and monitored levels of microbial aerosols were below those in residential environments that have been characterized through cross-sectional studies.

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Table I. Measurement parameters and methods.

Parameter	Sample collection method	Analysis method	Reference
<i>ETS contaminants</i>			
Carbon monoxide	continuous monitor	solid polymer electrolyte	11
Nicotine	sodium-bisulfate treated filter	gas chromatography--nitrogen selective detector	12
Respirable particles (integrated)	filtration with cyclone separator	gravimetry	12
Respirable particles (continuous)	continuous monitor	nephelometry	13
<i>Microbial aerosols</i>			
Fungi	impaction	culture/microscopy	14
Bacteria	impaction	culture/microscopy	14
<i>Pollutants</i>			
Ozone	MBTH*-coated filter	spectrophotometry	15
Carbon dioxide	detector tube	length of stain	16
<i>Other parameters</i>			
Temperature	continuous	platinum RTD	17
Relative humidity	continuous	thin-film dielectric sensor	17
Barometric pressure	continuous	piezoresistance	17
Air exchange	sorbent tube (passive)	gas chromatography of perfluorocarbon tracer (PFT)	18

\* 3-Methyl-2-benzothiazolinone.

Table II. Levels of ETS contaminants on smoking and nonsmoking flights.

Parameter	Smoking flights				Nonsmoking flights	
	Smoking	Boundary	Middle	Remote	Rear	Middle
<i>Particle-phase measurements</i>						
Average RSP (gravimetric) ( $\mu\text{g}/\text{m}^3$ )	174.6	67.5	42.5	52.1	59.3	69.4
Average RSP (optical) ( $\mu\text{g}/\text{m}^3$ )	177.0	39.7	18.8	17.9	10.3	10.6
Average RSP (both methods) ( $\mu\text{g}/\text{m}^3$ )	175.8	53.6	30.7	35.0	34.8	40.0
Average of peak RSP (optical) ( $\mu\text{g}/\text{m}^3$ )	833.4	211.8	68.7	69.6	18.2	16.4
<i>Gas-phase measurements</i>						
Average nicotine ( $\mu\text{g}/\text{m}^3$ )	13.43	0.26	0.04	0.05	0.0	0.08
Percent nicotine samples below minimum detection	4.3	54.4	82.6	66.7	100.0	78.3
Average CO (ppm)	1.4	0.6	0.7	0.8	0.6	0.5
Peak CO (ppm)	3.4	1.4	1.7	1.6	1.3	0.9

Table III. Levels of other pollutants on smoking and nonsmoking flights.

Parameter	Smoking flights		Nonsmoking flights
	Smoking rows	Middle rows	
Average CO <sub>2</sub> (ppm)	1562	1568	1756
Percent CO <sub>2</sub> samples $\geq$ 1000 ppm	87.0	88.1	87.0
Average ozone (ppm)	0.01	0.01	0.02
Percent ozone samples $\geq$ 0.1 ppm	0.0	0.0	0.0
Average bacteria (CFU/m <sup>3</sup> )	162.7	131.2	131.1
Average fungi (CFU/m <sup>3</sup> )	5.9	5.0	9.0

# REMOVAL OF GASEOUS INDOOR AIR CONTAMINANTS BY COMMERCIAL AIR FILTERS

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## ABSTRACT

The use of effective air cleaners provides one means to reduce indoor air contaminant concentrations. A series of commercial air filters was evaluated to determine their ability to remove gaseous contaminants from indoor air. Environmental tobacco smoke (ETS) was used as the test matrix because it contains many of the compounds which are typically present in indoor air. Concentrations of CO, NO, NO<sub>2</sub>, Total VOC (by FID detector), formaldehyde, nicotine, and 3-ethenylpyridine were determined. The data for each filter/compound combination were analyzed using a recently developed model for determining clean-air delivery rates. Results of the study demonstrated that significant removal of VOCs from indoor air can be accomplished through the use of sorbent-based air filtration systems. However, performance of sorbent systems varied across manufacturer and compound class. A reactive substrate designed for the removal of formaldehyde was effective, but its use resulted in the oxidation of NO to NO<sub>2</sub>. These results suggest that if reactive removal mechanisms are used, the potential effect of reaction byproducts on IAQ must also be addressed.

## INTRODUCTION

Air cleaners and filtration equipment can play an important role in maintaining good indoor air quality. Filters have long been used for removal of particulate contaminants from indoor air, and many types of filter media are also available for removal of gas-phase compounds as well. Filtration equipment can be used to remove general or specific classes of compounds and odors. Filtration may provide a viable alternative to increased ventilation in areas of a building with increased contaminant loads or specific problem contaminants or odors.

The ability of a filtration device to remove particulate phase compounds is addressed in several standards (1,2). One method has been developed to test the ability of an air cleaner to remove particles under actual use and provides a good estimate of expected performance under actual operation conditions (1). However, there isn't a similar straight forward method to evaluate the ability of filtration devices to remove gas-phase compounds from indoor air. To address this need, a new method to determine one performance criterion, the clean air delivery rate (CADR), was developed (3). (The CADR of an air cleaner is the equivalent volume of contaminant free air discharged by the cleaner. An air cleaner with a CADR of 100 CFM would have the same effect on contaminant concentrations of adding 100 CFM contaminant free air to the room.) The newly developed method for determining CADR can be applied to vapor phase compounds and is performed under actual operating conditions. The new method was used to compare the ability of several commercial air filters to remove gas-phase compounds from the air.

## EXPERIMENTAL

### Determination of Clean Air Delivery Rates (CADR)

Clean air delivery rates were determined by application of a phenomenological model for the behavior of gas-phase compounds in indoor air. A detailed derivation of the model appears elsewhere (3). Simply, the model assumes that the concentration of a contaminant at some time,  $t$ , can be described by an equation of the form:

$$\frac{dC(t)}{dt} = A(t) - k_r \cdot C(t) \quad (1)$$

where  $A(t)$  is the generation rate of the contaminant at time  $t$ .

If one makes the simplifying assumptions that the generation rate is constant and the component follows a first order decay process, then it is possible to solve for the concentration at any time,  $t$ .

$$C(t) = \frac{A}{k_r} \cdot [1 - e^{-k_r t}] + C_0 e^{-k_r t} \quad (2)$$

If the generation term is known, then it is possible to determine a solution for  $k$  by non-linear regression. Alternatively, at  $t \rightarrow \infty$ , the rate of generation will be equal to the rate of decay; i.e., the system will be at a steady state. The ratios of two steady state concentrations can be combined to yield the following equation:

$$\frac{C_{1,\infty}}{C_{2,\infty}} = \frac{k_{r2}}{k_{r1}} \quad (3)$$

$C_{1,\infty}$  and  $C_{2,\infty}$  can be determined experimentally. If  $k_{r1}$  is the decay rate of a component with no air cleaner in operation, then  $k_{r2}$  can easily be determined. The additional removal rate due to the air cleaner is simply the difference between  $k_{r1}$  and  $k_{r2}$ . The rate constant also can be expressed in CFM. Then, the difference between the rate constants is the CADR of the air cleaner.

### Environmental Chamber

The experiments were carried out in a newly constructed 45-m<sup>3</sup> environmental chamber. The chamber is constructed of stainless steel with a baked enamel finish on the interior walls. Illumination is provided by variable fluorescent and incandescent lights. Air is cooled or heated and humidified in an air handler within the chamber which recirculates chamber air at  $\approx 1500$  CFM. As much as 450 CFM of makeup air also can be introduced into the chamber through the air handler. The makeup air is dehumidified and passed through HEPA and charcoal filters before introduction into the room. Ventilation, temperature and relative humidity can be accurately and reproducibly controlled within the room. Air is drawn from the room for analysis through a teflon tube and sampling ports are located along one wall of the room.

Real-time determinations were made of CO (Thermo Electron Model 48, Franklin, MA), NO<sub>x</sub> (Thermo Electron Model 42, Franklin, MA), VOCs by FID (Combustion Engineering Model 8401, Ronceverte, WV). In addition, nicotine and 3-ethenylpyridine were collected on XAD-4 sorbent tubes (SKC Inc. Eighty-four, PA) and analyzed by GC with NPD detection (4,5), and

formaldehyde was collected on 2,4-DNPH-impregnated Sep-Paks (Waters Chromatography Part 37500, Milford, MA) and determined by HPLC with UV detection.

Smoke was generated by a smoking machine located in the chamber. Following a 15-minute background collection period, two pairs of cigarettes were smoked in sequence to rapidly elevate smoke concentrations in the room to near steady state. For the remainder of the experiment, individual cigarettes were burned continuously. The smoke concentration in the room remained steady from 50-140 minutes (see Figure 1). Sampling for nicotine, 3-ethenylpyridine and formaldehyde was performed during this period. The 50-140 minute period was also used for determining the average concentration of analytes measured by real-time monitors.

#### Air Cleaners

Smoke particles were removed from the room by an electrostatic precipitator. This was done to protect the filter media from particle build-up. The fan in the electrostatic precipitator was also used to force air through the various filter media. The different filters used are described in Table I. Filter media were obtained from three different manufacturers. All three panel filters were partial-bypass filters. Bypass filters allow some air to pass through, without coming in contact with the adsorbent media. The bed filters contain adsorbent-filled panels through

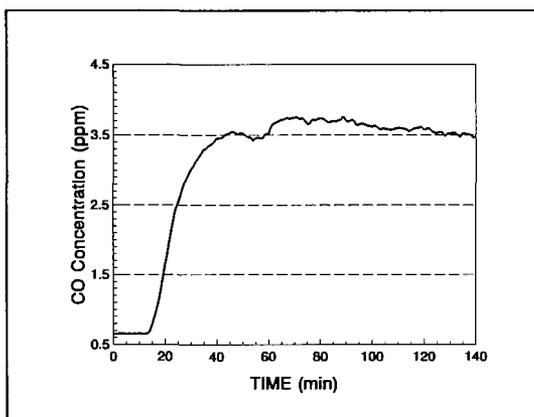


Figure 1. Real-time CO concentration for the Control condition. Sampling/averaging time for determining analyte concentrations is indicated on the figure.

Table I. Description of filters evaluated. Filter type, media, number of tests using filter, and CO concentration during averaging period with each filter in use are shown.

Identifier	Type	Filter Area (ft <sup>3</sup> )	Filtration	# of runs	CO (ppm)
PF1	panel	1	1" carbon	4	3.17
PF2	panel	1	2" carbon	2	3.19
PF2b	panel	1	2" carbon	2	3.31
BC	bed	5.5	½" carbon	1	3.02
BCC	bed	11	½" carbon X 2	5	3.05
BPC	bed	11	½" permanganate ½" carbon	3	3.02
BPA	bed	11	½" permanganate ½" acid-treated carbon	3	3.14
Control	N/A	N/A	None	4	2.95

which all the air must pass. The large surface area of these filters decreases the face velocity across the panels, which results in an increased residence time for air passing through the filter.

The manufacturer of the bed filters provided the electrostatic precipitator and a housing to hold the media beds. A 12" x 12" box was constructed to hold the panel filters. The bed filters were installed downstream from the electrostatic precipitator in the order shown in Table I; e.g., the permanganate-containing bed was installed upstream from the carbon bed in the BPC arrangement. "Cleaned" air was directed through a piece of flex-duct into the recirculation inlet of the air handler. This was done to minimize the likelihood of short-circuiting of air between the outlet and inlet of the air cleaner. Air flows were determined by performing a five-point traverse of the inlet duct with a hot-wire anemometer, averaging the five-flow rates, and converting linear velocity to volumetric flow. The fan velocity was adjusted to give a 500 CFM flow through the filters. The electrostatic precipitator was not operated during the Control sessions; however, it was continuously operated during filter test sessions.

Table I also shows the number of runs performed with each type of filter media and the CO concentration during the averaging period (50-140 min). The CO concentrations in the table show that similar amounts of ETS were generated in each of the tests. Thus, differences in concentration of other analytes are predominantly due to the effect of the filtration equipment rather than differences in smoke production between runs.

## RESULTS

Because the removal efficiency of any filter will vary for different types of contaminants, it is necessary to determine the CADR for each compound of interest. CADRs for each air filter and analyte tested are summarized in Table II. The efficiency of the filter media can be determined by dividing the CADR in the table by the flow-rate of air through the filter (500 CFM). It can be seen that efficiency varies with both analyte and type of filter media. Negative CADRs indicate that the concentration of the given compound *increased* when that particular type of filter media was used. Physically, this indicates an effective decrease of ventilation to a space with respect to that particular compound. The results for each compound are discussed in more detail below.

Table II. Clean air delivery rates (CADR) for each analyte measured by media type. One-pass filter efficiency can be calculated by dividing the CADR by 500 CFM.

Filter	VOC	Nicotine	3-Ethethyl-pyridine	Formaldehyde	NO <sub>x</sub>	NO	NO <sub>2</sub>
PF1	88	83	120	-57	NR	39	-107
PF2	124	111	248	-50	NR	26	-74
PF2b	197	98	239	NR	NR	NR	NR
BC	229	189	389	53	79	79	27
BCC	296	235	459	89	91	93	65
BPC	255	214	454	192	166	357	-87
BPA	199	227	391	137	118	249	-92

### **Volatile Organic Compounds**

The FID gives a response proportional to the total VOC concentration in the room. Although this detector is non-specific for particular classes of compounds, the results are indicative of the filter's ability to remove general organic compounds from the air. Each type of filter media was effective at removing VOCs from the air in the chamber. In general, increasing filter thickness and the amount of carbon present in the filter lead to increased efficiency. There may also be some effect of charcoal type. The use of a permanganate-impregnated media appeared to remove some VOCs (BC vs. BPC). Phosphoric acid-impregnated charcoal reduced the removal of VOCs by the filter (BPA vs. BPC). It is likely that impregnation reduced the number of pores available in the charcoal that could serve as adsorption sites.

### **Nicotine**

Previous studies have shown that nicotine is surprisingly difficult to remove from the air with filtration equipment (3). For each of the filters tested here, the removal of nicotine was not as efficient as the removal of general VOCs. The one exception involves the use of acid-treated charcoal. Nicotine is a gas-phase base; reaction with phosphoric acid in the filter leads to the formation of a non-volatile salt. However, the use of a permanganate-treated filter appeared to have as great an effect on the removal of nicotine (BPC vs BC) as the use of an acid-treated filter (BPC vs BPA). The use of significant quantities of carbon would appear to be the best way to remove this compound from indoor air.

### **3-Ethenylpyridine**

When tobacco is burned, nicotine is pyrolyzed. One product of this pyrolysis is 3-ethenylpyridine. Whereas nicotine demonstrated a poorer removal rate than VOCs in general, all the filters were much more efficient at removing 3-ethenylpyridine than they were at removing VOCs in general. The removal efficiency exceeded 90% for the BCC filter. Once again, quantity of charcoal appears to be the most significant factor in predicting the removal of this compound from the air. Results for this compound further demonstrate that one cannot predict the removal of specific compounds based on a general indicator.

### **Formaldehyde**

In general, carbon filters are not efficient at removing formaldehyde from the air. This can be seen in the results presented in Table II. PF1 and PF2 appear to have led to an increase in the formaldehyde concentration in the room. Some of the increase may be due to slightly higher smoke levels in the room when this filter was in use (see Table I). However, it also appears that some off-gassing of formaldehyde from the sorbent or filter construction materials may have occurred. PF2b did not remove formaldehyde from the air. The carbon-bed filters removed a small amount of formaldehyde. Permanganate-impregnated filters remove formaldehyde by oxidation. Reasonably efficient removal of formaldehyde was demonstrated by the permanganate-containing filters (BPC, BPA). Unlike the plain charcoal beds (BC, BCC), the acid-treated charcoal was ineffective at removing formaldehyde from the air.

### **Oxides of Nitrogen**

If one examines the CADRs for  $\text{NO}_x$ , a mistaken impression of the behavior of the filters can be obtained. Neither the PF1 nor the PF2 filters removed  $\text{NO}_x$ . However, both filters appear to have removed NO from the air by oxidizing it to  $\text{NO}_2$ . The carbon-bed filters removed a small amount of both NO and  $\text{NO}_2$  from the air. The permanganate-containing filters removed NO efficiently, but they did so in part by oxidizing NO to  $\text{NO}_2$ . Although the permanganate-containing filter was relatively efficient at removing  $\text{NO}_x$  and quite efficient at removing NO, it did so by generating a less desirable compound,  $\text{NO}_2$ . A potential exists for generating unknown and/or undesirable reaction products with oxidative filter media. When using such media, one

must be careful to ensure that the removal of one compound does not result in the generation of less desirable compounds in an enclosed space.

## CONCLUSIONS

Air cleaners can be effectively used to remove a wide range of compounds from indoor air. Commercial filters differ greatly in their ability both to remove various amounts and to select particular classes of compounds for removal from air. Performance criteria such as CADR can be used to help determine the best filter for an application. CADRs also can be calculated for compounds whose concentrations in air cannot be determined in real-time.

Because some air filters/cleaners operate by reacting with species in indoor air, one must be careful to determine that undesirable species are not being formed as byproducts of such reactions. A general knowledge of the effect of a filter on indoor air quality does not alleviate the need for testing a filter to determine its effect on the concentration of specific compounds.

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*Session 7*

*Measurement Methods Development*

# FAST ANALYSIS OF C<sub>2</sub>-C<sub>12</sub> AMBIENT AIR HYDROCARBONS USING A MULTI-COLUMN GAS CHROMATOGRAPHIC SYSTEM

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## ABSTRACT

A method has been developed for the speciation of C<sub>2</sub>-C<sub>12</sub> hydrocarbons (HC) in ambient air without employing subambient temperature programming. A ten-port valve was used for cryogenic concentration of sample air as well as column switching in a three-column system housed in a single GC oven. The C<sub>2</sub>-C<sub>8</sub> hydrocarbon fraction was analyzed concurrently with >C<sub>8</sub> fraction and detected by separate flame ionization detectors. Analysis time was approximately 30 minutes.

## INTRODUCTION

HC in ambient air are ozone precursors. The main sources of these compounds in an urban environment are emissions from automotive and stationary sources as a result of incomplete combustion and evaporation of fuels and solvents. Speciated HC data are essential to the running of photochemical models that are used by air pollution control agencies in formulating ozone control strategies. Under the 1990 Clean Air Act Amendments, the USEPA mandates these agencies in serious, severe, or extreme ozone non-attainment areas to establish Photochemical Assessment Monitoring Stations (PAMS) which monitor routinely speciated HC among other parameters.

Gas chromatography has been used for the measurement of ambient air HC. Because they exist at low levels, it is necessary to concentrate the sample using either solid sorbents or cryogenic means prior to analysis. Earlier methods employed several chromatographs, each designed to speciate a certain fraction of the sample HC. In one such approach, the C<sub>2</sub>-C<sub>5</sub> aliphatic, the C<sub>4</sub>-C<sub>8</sub> aliphatic, and the C<sub>6</sub>-C<sub>11</sub> aromatic and aliphatic components were determined by analyzing separate aliquots of a sample (Lonneman et al. 1974<sup>1</sup>; Westberg et al. 1984<sup>2</sup>). Other approaches involved two analyses for the light and heavier fractions respectively (Dimitriades and Seizinger 1971<sup>3</sup>; Rasmussen et al. 1974<sup>4</sup>; Singh 1980<sup>5</sup>; Grosjean and Fung 1984<sup>6</sup>; Stump and Dropkin 1985<sup>7</sup>). These approaches have the disadvantages of needing additional gas chromatographs, sample concentrators, and data systems in order to process the samples efficiently.

The development of these various approaches reflects improvements in column technology through the years. Packed and capillary columns with coated stationary phase have been replaced by high resolution bonded phase fused silica capillary columns. Seila and Lonneman (1988<sup>8</sup>) performed the analysis of C<sub>2</sub>-C<sub>12</sub> HC with a single column albeit needing sub-ambient temperature programming for separation of the C<sub>2</sub> components. However, the C<sub>2</sub> separation is not always ideal as these researchers have experienced. A thick film (low

phase ratio) column that is needed to achieve good C<sub>2</sub> separation is not efficient for the heavy components. Consequently, analysis time is prolonged due to the necessity of starting at a sub-ambient oven temperature (~ -60°C) and finishing at a high temperature. Returning the oven to the initial conditions also takes some time and increases cryogen use. Recycle time is in excess of an hour.

There have been continual interests in a gas chromatographic system for the speciation of ambient HC with minimal need for cryogen. Such systems in automatic form, for example, would be useful in gathering the much needed HC data in remote areas for the operational and diagnostic evaluation of large scale acid deposition models like Regional Acid Deposition Model and Acid Deposition and Oxidant Model. PAMS will also be benefited because excessive demand for cryogen increases considerably the operating costs and creates difficulties in supply logistics. The present method was developed to limit cryogen use and shorten analysis time without sacrificing performance and resolution. The method has been under evaluation for the past several years, and applied to the analysis of ambient air samples from the rural areas of the eastern United States and urban samples in California.

## EXPERIMENTAL METHODS

Chrompack (Raritan, NJ) pioneered the use of a Porous Layer Open Tubular (PLOT) column with an internal deposit of Al<sub>2</sub>O<sub>3</sub>/KCl for analysis of hydrocarbons. The column can separate methane and the C<sub>2</sub> species at ambient conditions. However, its usefulness is limited by an upper temperature limit of 200°C, at which the >C<sub>8</sub> HC can only be analyzed isothermally. To utilize this column effectively, a three-column switching system incorporating a 10-port valve (Valco, Austin TX) as shown in Figure 1 was devised. Columns 1A and 1B are non-polar, methyl silicon capillary columns ( 0.18mm I.D., 0.4μ DB-1, 15-m, and 25-m respectively from J. & W. Scientific, Folsom, CA), and Column 2 is a 50-m 0.32mm I. D. alumina PLOT column. The freeze-out loop, and Sample In and Out ports in the diagram may represent any sample concentration device connected to these ports. In our case, a glass-bead packed freeze-out loop for use with liquid Ar and a volume transfer apparatus (Grosjean and Fung, 1984<sup>5</sup>) for assessing the freeze-out air volume were connected. Carrier 1 and 2 were pressure-controlled, and were set to obtain a linear velocity of ~40cm/sec. with hydrogen. Restrictors were employed to balance the flow streams to avoid baseline disturbances during valve switching.

The system was operated as follows: A sample aliquot was concentrated in valve Position 1, and injected into the GC via switching to Position 2 and heating the loop with boiling water. With the oven held initially at 23°C, only the heavy HC components in the sample entering Column 1A were retarded. The fast eluting species in Column 1A were transferred to, and separated by Column 2 (PLOT). At the appropriate time, the valve was returned to Position 1, placing Column 1A in series with 1B, thereby allowing the residual (retarded) components in Column 1A to continue with the separation in Column 1B. Also, another sample could be concentrated at this point while the analysis was still in progress.

To arrive the proper valve switching time, HC standards were analyzed isothermally with Column 1A to determine the retention times of components, about which a cut was to be made. Then the column was installed into the valve and tested again with standards to fine tune the split time. The analysis was performed with a Hewlett-Packard 5890 Series II gas chromatograph with dual flame ionization detectors. The GC's Valve Programming feature

was used to control the operation of the valve. Data were processed with a dual channel Shimadzu CR-4A integrator.

Detector response was calibrated using NIST SRM 1805, a 254 ppb benzene in nitrogen. By altering the valve switch time, benzene can be directed to either the PLOT or DB-1 column for that purpose. In analysis of ambient HC, it is assumed that all HC respond in the FID in proportion to the number of carbon atoms, and concentrations of the components are reported on a ppbC basis.

## RESULTS and DISCUSSION

Figure 2 is a chromatogram of ambient air C<sub>2</sub>-C<sub>12</sub> hydrocarbons analyzed using a 50-m 0.32mm I.D. nonpolar (Chrompack CP-Sil 5 CB) capillary column with sub-ambient temperature programming. The stationary phase was too thin to provide good C<sub>2</sub> separation. The peak at 4.04 min. represents unresolved ethylene and acetylene, and the peak at 4.24 min., ethane. The analysis time is ~50 min., typical for this approach.

With a 15-m short column and an ambient oven temperature, the peaks in the first 20 min. of the chromatogram in Figure 2 would elute unresolved. Compounds up to n-heptane eluting off Column 1A were found to have transferred to the PLOT column when the valve was held in Position 2 for 2.5 min. Then the valve was returned to Position 1, and the oven temperature increased to resolve the components.

The precut after n-heptane represents an optimal choice because there is a wide gap before the next significant peak, methylcyclohexane, elutes. There is little likelihood of peak splitting making a cut at that point. Also, the cut allows the PLOT column to be utilized most efficiently. Unlike a methyl silicon column, which separates compounds by boiling point, the alumina column separates according to polarity. Branched alkanes of the same carbon number elute closely as bundles, followed by the corresponding n-alkane, and then the bundles of corresponding olefins. Benzene elutes after n-heptane. Therefore, unknown peaks can be readily classify by class and carbon number. Extracting such information is not possible from an analysis performed with a DB-1 column. To a photochemical modeler, having unknown peaks classified provides valuable information about the sample, and is, thus, much better than if the peaks are left unclassified.

The elution of acetylene apparently varies with the state of deactivation of alumina by water in the sample. The compound has been found eluting after propylene to after n-butane. Under the present analytical conditions, acetylene elutes mostly after n-butane, although there had been occasions in which it was unresolved from n-butane. Reportedly, Chrompack has some success in solving this problem by replacing the KCl in alumina with Na<sub>2</sub>SO<sub>4</sub>.

Since both the DB-1 and PLOT columns were housed in the same oven, experimentation was needed to arrive a temperature program for optimal elution of the components concurrently. The analytical conditions were as follows:

Initial: 23°C, isothermal for 2.5 min.

Rate: 10°/min. to 40°

4°/min. to 100°

9°/min. to 195°, isothermal at 195° for 5 min.

Valve: 0 min. ON; 2.5 min. OFF.

An ambient air sample from Oildale, CA was analyzed using this approach. The resulting chromatograms are shown in Figure 3A and 3B. Except for the lack of olefins and absence of acetylene, this samples, being from a area of petroleum production, is considerably more complex than a typical ambient air sample. Over 250 peaks were detected. Excellent resolution was evidenced by the partial resolution of m- and p-xylene. Analysis was completed in approximately 30 minutes. The remaining few minutes of the temperature program was to ensure the PLOT column starting the next run at a consistent state of activation. The shortened analysis time is the direct result of being able to separate the sample HC into the light and heavy fractions and perform the speciation of each fraction simultaneously. In addition, by virtue of the valve position, cryogenic concentration of another sample can occur while analysis is still in progress. This would be important if automated analyses were to be performed on an hourly basis, as stipulated under the PAMS network.

The method has been used to analyzed standards and ambient air samples in informal interlaboratory comparisons with several other laboratories, which included the USEPA Gas Kinetics & Photochemistry Research Branch, and Desert Research Institute. The results were in good agreement, indicating no deficiency existed with the method.

## CONCLUSIONS

A method has been developed for the analysis of ambient air HC without the use of sub-ambient temperature programming. The method showed comparable results to the traditional methods, but reduced the analysis time significantly to approximately 30 min. without sacrificing resolution and performance.

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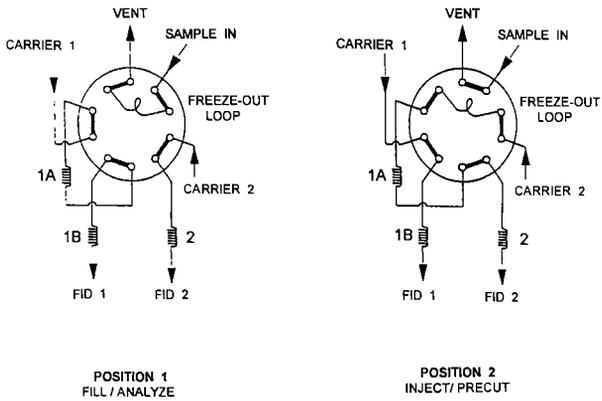
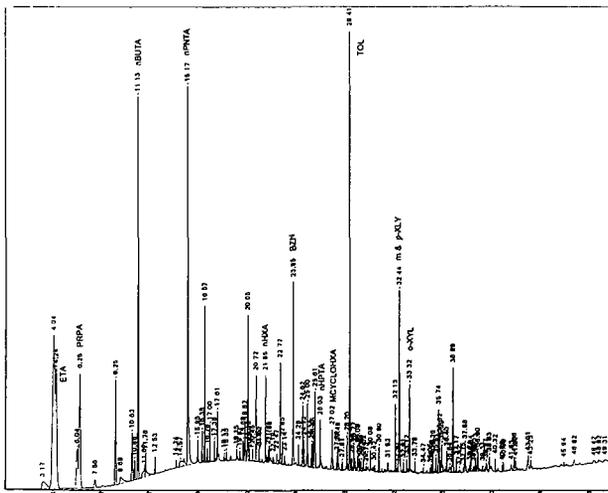


Figure 1: Valve Configuration for Analysis of Ambient Air Hydrocarbons



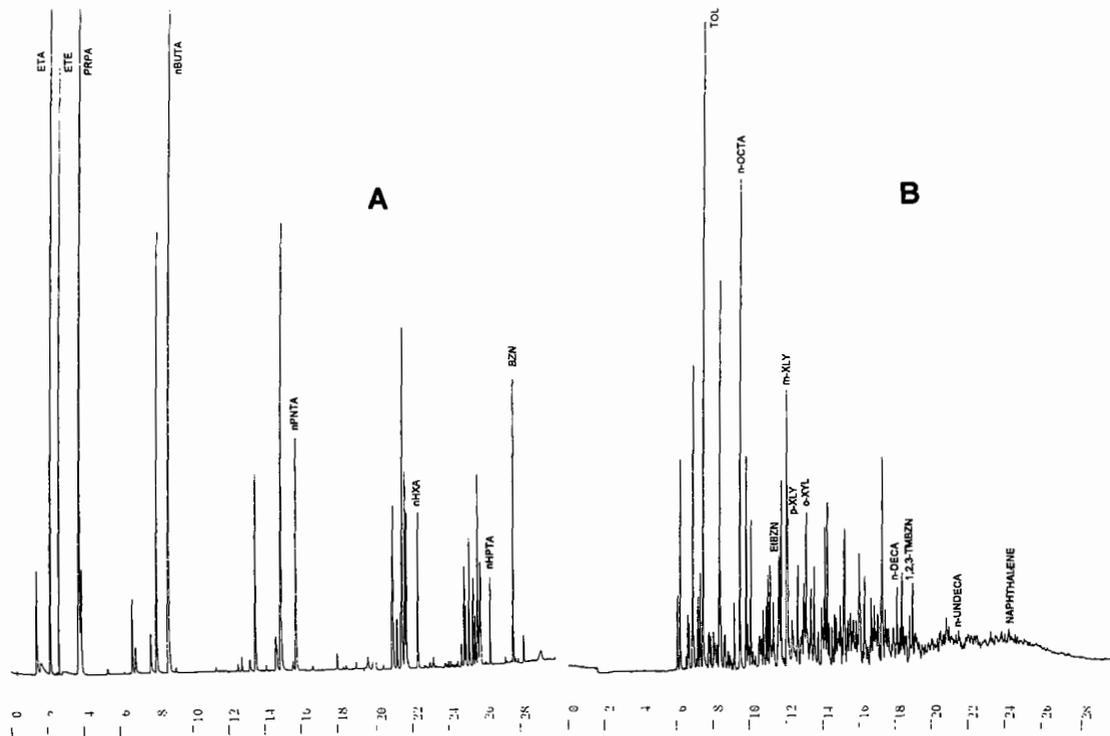


Figure 3: Analysis of Ambient Air Hydrocarbons Simultaneously Using an Alumina PLOT and DB-1 Column: A - PLOT Column; B - DB-1 Column

**TESTING AND EVALUATION OF 2 PROTOTYPE DEVICES FOR  
DIRECT MEASUREMENTS OF AIR-WATER TRANSFER PROCESSES  
INVOLVING TOXIC CHEMICALS**

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**ABSTRACT**

Among the environmental pollutants of concern in most jurisdictions in North America are many volatile and semi-volatile organic compounds. Their vapor-phase fractions partition themselves between the atmosphere and other environmental compartments (water, soil, biomass). Determinations of the magnitude and direction of the mass transfer fluxes of toxic chemicals between the atmosphere and the hydrosphere constitute an important topic in current scientific research. Two prototype devices for direct measurements of air-water exchange processes have been built and tested under laboratory conditions. One is a sparger device which can be used to establish the (truly) dissolved concentration of a given chemical in water, and hence its potential for diffusive transfer at the air-water interface. The other device is a flux monitor with which the chemical mass transfer rate from the water surface to the atmosphere (or vice versa) can be measured. The paper describes the equipment as well as the sampling and analytical methods development completed so far, and presents initial results from laboratory testing of the two devices.

**INTRODUCTION**

The importance of atmospheric transport and deposition (wet &/or dry) as environmental pathways for the input of persistent organic contaminants known to occur in the Great Lakes ecosystem has been recognized for more than a decade (Eisenreich et al.<sup>1</sup>; IJC<sup>2</sup>; Schroeder & Lane<sup>3</sup>; Swackhamer & Hites<sup>4</sup>). Aside from efforts dedicated to improving our understanding of vapor phase--particle phase partitioning of semi-volatile organic compounds in the atmosphere (Bidleman et al.<sup>5</sup>; Pankow<sup>6</sup>; Lane et al.<sup>7</sup>) researchers in the Great Lakes scientific community (and elsewhere) are acutely interested in advancing the current state of knowledge surrounding the mass transfer of persistent organic substances across the air-water interface (Mackay et al.<sup>8</sup>; Sproule et al.<sup>9</sup>; McConnell et al.<sup>10</sup>). Whereas wet and dry (atmospheric) deposition processes are uni-directional (resulting in the transfer of chemicals from the atmosphere to the water surface), air-water exchange processes are bi-directional in nature (mass transfer being either "positive" or "negative" by convention) with the magnitude and direction of the net chemical "flux" determined by various parameters, including: (a) physico-chemical properties of the substance (e.g. vapor pressure and water solubility -- whose ratio make up the Henry's Law coefficient); (b) the relative concentrations of the chemical in the water and air compartments (i.e. the degree of "oversaturation" or "undersaturation" in a given compartment), and (c) environmental conditions (e.g., air/water temperature, wind speed/turbulence, nature and extent of bubble formation, presence or absence of a microlayer of surface film) which influence water-side or air-side mass transfer coefficients. To understand, and ultimately model or predict, the movement and eventual fate of toxic chemicals released into the environment (Schroeder & Lane<sup>3</sup>), it is essential that we advance our knowledge of air-water exchange processes, especially the rates of deposition, absorption, diffusion, and evaporation/volatilization.

Estimation, or (even better) direct determination, of the magnitude and direction of the fluxes of persistent organic pollutants between the atmosphere and surface waters (oceans, lakes, rivers, reservoirs, impoundments) represent an important topic in contemporary scientific research. On the many lists of priority toxic substances drawn up by various levels of government and other organizations/institutions or judicial bodies in the United States, Canada, and other industrial nations, there are numerous volatile and semi-volatile organic compounds (VOCs & SVOCs) including chlorinated alkanes/alkenes/benzenes, organochlorine pesticides, and polychlorinated biphenyls (PCBs). Many of these persistent chemicals are present in natural waters, including those of the Great Lakes.

To address research goals and objectives outlined in the 1987 Protocol to the U.S.- Canada Great Lakes Water Quality Agreement (Annex 15: Airborne Toxic Substances), a collaborative project involving government, university, and private sector scientists from Canada and the United States has been initiated for the purpose of studying air-water exchange processes involving priority toxic chemicals. In this project, research is being conducted on the development, evaluation, and application of two types of experimental apparatus with the potential for making direct (*in situ*) measurements of air-water exchange processes and transfer rates. Two devices -- a sparger and a flux monitor -- were built and have been tested under controlled laboratory conditions. This paper describes the prototype equipment and presents results from sampling and analytical methods development, as well as laboratory testing and evaluation of the equipment. The target compounds tentatively selected for the first phase of our project, namely chloroform, 1,3-dichlorobenzene, alpha- and gamma-hexachlorocyclohexane (lindane), and 2,4,6-trichlorobiphenyl, constitute a sub-set of the compounds of interest for which Henry's Law coefficients have been provided in Table I.

## EXPERIMENTAL SECTION

### Equipment and Design Considerations

For the first phase of this project, the sparger apparatus described by Sproule et al.<sup>9</sup> was re-designed to promote: (a) improved water exchange characteristics (through the flow holes), and; (b) better internal circulation of bulk liquid so as to prevent significant depletion of the target chemical(s) from the water column being contacted ("equilibrated") with the sparging gas (air). Figure 1 shows the prototype sparger device which was fabricated from virgin grade Teflon<sup>®</sup> (to minimize sorption/loss of chemicals on the surfaces of the construction material) and was subsequently evaluated in the laboratory (at the University of Toronto). The exit stream passed through a glass tube containing an adsorbent bed of Tenax T.A. which efficiently retains the chlorinated organic target compounds.

A flux monitor was designed and constructed for this project by Concord Environmental Corporation (Toronto). This device is intended to be used, along with the sparger, in future investigations of mass transfer of toxic chemicals across the air-water interfacial boundary. Design criteria established for this device were: (a) large collection area, small internal volume, and low dilution flow rate so as to optimize the sensitivity of the system; (b) efficient mixing of target compounds with purge gas (air) in the monitor chamber; (c) good stability on an open water surface under moderate wind and wave conditions; (d) minimal chemical losses on interior surfaces of the monitor; (e) minimal perturbation of environmental variables such as light intensity/spectral distribution, temperature, and barometric pressure; (f) easy to interface with integrative sampling devices (adsorbent tubes).

The prototype unit of the flux monitor is depicted in Figure 2. It consists of a tubular frame made of 1.27 cm (1/2") schedule 80 PVC pipe fastened with metal Kee Klamps<sup>®</sup>. The top surface is a 1.27 cm thick transparent cast acrylic sheet with a hole drilled in each corner for fitting the PVC pipe. The acrylic sheet is held in place by hose clamps, which allow the height of the monitor to be adjusted. Attached to the outside of the 1.27 cm thick acrylic skirt were four floats ("boat fenders") to provide buoyancy. The monitor chamber consists of a clear Mylar<sup>®</sup> film which is attached to the acrylic skirt at the bottom and the acrylic sheet at the top. The truncated pyramid-shaped monitor covers a surface area of 0.194 m<sup>2</sup> and contains a volume of 24.3 L. Ultra zero air (Matheson Gas Products Canada) was used as the purge gas.

## RESULTS AND DISCUSSION

### Laboratory Tests

**Sparger.** Tests were performed with this apparatus in a Nalgene<sup>®</sup> tank containing approximately 700 L of water spiked with monochlorobenzene to a concentration of 10 micrograms/liter. Sparging gas (ultra zero air) flow rate was 0.3 L/min for experiment durations of about 30 minutes. Samples were thermally desorbed from the trap into a gas chromatograph (HP 5890 equipped with a flame ionization detector) using an Environchem Unacon Series 810 thermal desorption system. Helium (UHP grade) was the carrier gas. A typical gas chromatogram is reproduced in Figure 3.

**Flux Monitor.** Tests were conducted at Concord Environmental Corp. with 4 target compounds added to a plastic pool containing approximately 100 L of water. The concentrations of the target compounds were:

Chloroform:	258 ng/L	Dichlorobenzene:	14.8 µg/L
Lindane:	687 ng/L	2,4,6 - PCB:	211 ng/L

After spiking and stirring the water, the flux monitor was placed on the water surface and a purge flow of 1.1 L/min was used to flush the chamber. The exit air was split into 2 streams, each of which was drawn through an adsorbent tube (packed with 300 mg sequential plugs of 20/40 mesh Carbotrap<sup>®</sup> B and Carbotrap<sup>®</sup> C in 4 mm (i.d.) x 11.5 cm glass tubes) at a sampling flow rate of about 0.2 L/min for 60 minutes. Recovery of target compounds from exposed adsorbent tubes was performed either by solvent extraction, or by thermal desorption (using a Dynatherm Analytical Instruments, Inc. model 850 desorber and model 851 temperature controller). Three consecutive sets of duplicate samples were obtained. A representative gas chromatogram of a pentane standard solution containing four target compounds is shown in Figure 4.

### Sampling and Analytical Methods Development

The target compounds selected span a wide range of volatility, from extremely volatile (CHCl<sub>3</sub>) to semi-volatile compounds (e.g., PCBs). Collection on dual adsorbent-bed tubes was considered to be the method of choice, since few (if any) adsorbents quantitatively retain compounds with such a broad span of volatility. For recovering target chemicals from the adsorbents, eight solvents were compared: pentane, hexane, benzene, toluene, cyclohexane, carbon disulfide, and mixtures of toluene and pentane or hexane. Pentane proved most effective. Detection limits (for the solvent extraction - gas chromatography - electron capture detection method) and pentane extraction efficiencies are given in Table II. The sensitivity of this method was found to be insufficient for determination of the target compounds at concentrations likely to be encountered in field samples. Hence the analytical method was refined by replacing solvent extraction with a thermal desorption technique (resulting in a method sensitivity increase of nearly 500 times).

## CONCLUSIONS

Two distinctly different prototype devices -- for application in future field investigations of air-water exchange processes involving toxic organic substances known to be present in the waters of the Great Lakes -- have been built, tested and evaluated under laboratory conditions during the first phase of this research project. These tests have indicated some areas where improvements can be made, either to the prototype devices or to the sampling, sample handling/preparation and analytical methods which are to be carried forward to the next stage of this project (viz., field testing and intercomparison of the 2 devices).

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Table I. Henry's Law coefficients for compounds of interest.

Compound	H @ 25°C (Pa m <sup>3</sup> /mol)	Reference
Trichloro- methane (Chloroform)	320 283 (20°)	Lyman et al. <sup>11</sup> Mackay & Shiu <sup>12</sup>
1,3 - dichloro- benzene (m-xylene)	376	Shiu <sup>13</sup>
1,4 - dichloro- benzene (p-xylene)	160	Mackay & Shiu <sup>12</sup>
2,4,4' - tri- chlorobiphenyl (IUPAC no.28)	32	Dunnivant et al. <sup>14</sup>
2,4',5 - tri- chlorobiphenyl (IUPAC no.31)	13	Dunnivant et al. <sup>14</sup>
2,4,6 - tri- chlorobiphenyl (IUPAC no.30)	67	Dunnivant et al. <sup>14</sup>
α - hexachloro- cyclohexane	0.771 <sup>a</sup> 0.532 (20°)	McConnell et al. <sup>10</sup>
γ - hexachloro- cyclohexane	0.356 <sup>b</sup> 0.261 (20°)	McConnell et al. <sup>10</sup>

a: calculated from  $\log H = 2810/T + 9.31$

b: calculated from  $\log H = 2382/T + 7.54$

Table II. Detection limits and solvent extraction efficiencies for the pentane extraction - gas chromatography-electron capture detection method.

Compound	Detection Limit pg/injection	Extraction Efficiency (%)
Chloroform	5	95
1,3- Dichlorobenzene	50	86
Lindane	1	71
2,4-6- Trichlorobiphenyl	1	82

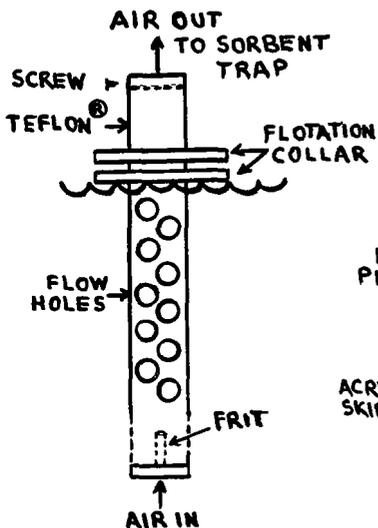


Figure 1. Prototype sparger.

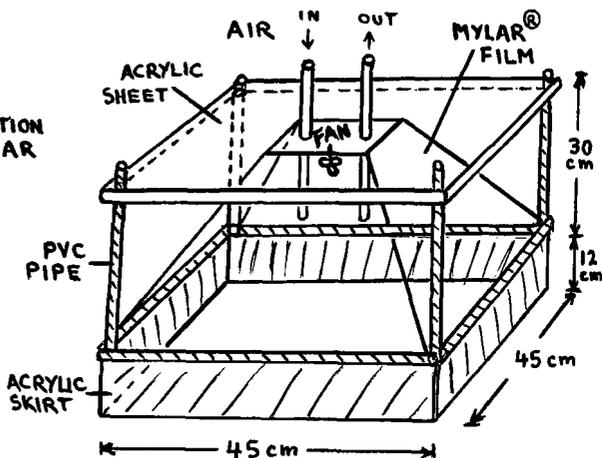


Figure 2. Prototype flux monitor.  
(Boat fenders not shown).

GC conditions	
Column =	DB-5 (30 m x 0.32 mm)
Inject. temp. =	300°C
FID temp. =	300°C
Temp. progr. =	65°C + 10°C/min for 4 minutes

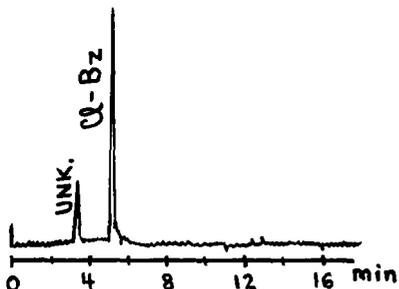


Figure 3. Chromatogram of sample obtained by sparging 10 L of air through water containing 10 µg/L of monochlorobenzene.  
("UNK." = unknown chemical).

GC conditions	
Column =	DB-17 (30 m x 0.25 mm)
Inject. temp. =	250°C
ECD temp. =	350°C
Carrier (He) =	1.6 mL/min
Temp. progr. =	40°C for 3 min 10°/min to 250°C

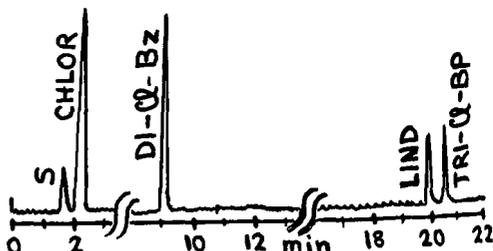


Figure 4. Gas chromatogram showing separation of four target compounds: chloroform, 1,3-dichlorobenzene, lindane, 2,4,6,-trichlorobiphenyl.  
(S = solvent (pentane) peak).

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## **A UNIVERSAL AIR PRECONCENTRATOR FOR AUTOMATED ANALYSIS OF AMBIENT AIR, STACK GAS, LANDFILL GAS, AND AUTOMOBILE EXHAUST USING GC/MS METHODS**

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### **ABSTRACT**

Today's Air Analysis laboratory is faced with the challenge of having to analyze a wide range of sample types and concentrations with limited analytical instrumentation. Most laboratories do not have a large enough sample load to dedicate a preconcentrator and GC/MS to a particular sample matrix. This can result in the need to replumb, or reoptimize the system when switching between ambient and source level samples, or when sample matrices are high in CO<sub>2</sub>. In addition, polar compounds may have a different optimum setup from that of the less polar TO14 compounds. Finally, even after reoptimizing for ambient level samples, each position of an autosampler manifold would have to be verified as clean before they could reliably be used for ppt-ppb level work once ppm level VOCs have been allowed to come in contact with surfaces and fittings.

A single preconcentration system has been developed that can perform analyses of high (ppm) and low (ppt-ppb) level samples using 16-position automation without the possibility of system contamination. Totally separate inlet systems are utilized to prevent ambient air samples from being exposed to surfaces that have contacted high concentration samples. Absorptive surfaces, such as Nafion dryers and Viton elastomeric valve sets and o-rings have been completely eliminated from the sample path to further reduce cross-contamination. Software selection of 1,2, or 3 stage preconcentrations can optimize performance for high or low level CO<sub>2</sub> matrices without any replumbing. Both polar and non-polar compounds are quantitatively concentrated and delivered into a GC/MS while removing most of the water and CO<sub>2</sub>.

### **SYSTEM DESCRIPTION**

The Entech 2000 Preconcentrator was designed to be both modular and software configurable to permit the analysis of the wide range of sample concentrations and matrices found in air monitoring. Up to three traps can be installed to concentrate samples, manage water and CO<sub>2</sub>, and then focus the concentrate at the head of the analytical column for high performance GC or GC/MS (FIGURE 2). Currently supported trapping module configurations are as follows:

Module 1	Module2	Module3
Nafion Dryer	Glass Bead Trap	On-column focuser
Bypass	Glass Bead Trap	"
Glass Bead Trap	Glass Bead Trap	"
Glass Bead Trap	Low Temp Adsorbent	"
Adsorbent trap	Adsorbent trap	Bypass

Each of these trapping procedures can be optimized for VOC preconcentrations based on technical as well as practical considerations. For example, when water management is not as important (as with GC/FID), a bypass followed by a glass bead trap is sufficient. For heavier, thermally stable compounds such as BTEX, a single tenax trap operated without focusing or cryogen will work very well. Cryogenless preconcentration of C2-C10 hydrocarbons and most of the Air Toxic compounds can be performed using 2-stage adsorbent trapping, first on a large diameter trap followed by further volume reduction on a narrower trap for faster desorption and better chromatography.

One hardware configuration listed can perform most of these trapping procedures just by changing how the preconcentration is allowed to proceed under software control. By installing a glass bead trap in the first stage and a tenax trap in the second stage, the system can be instructed to either trap initially on glass beads, or alternatively directly on the tenax trap by keeping the glass bead trap at 60 deg. C. To extend the trapping range of the tenax trap to include light VOC's, the temperature can be lowered to ambient to -50 deg. C, at which temperature vinyl chloride has over a 500 cc breakthrough volume. Optimum configurations for various sample types and matrices will be discussed individually in greater detail.

## FLEXIBILITY THROUGH SOFTWARE CONTROL

The 2000 preconcentrator software allows selection of preconcentration parameters by selecting a particular application. Applications available to the user are, in turn, dependent on their current hardware configuration. In addition to the selection of trapping modules listed, the user can indicate in the software which inlets or autosamplers are currently connected to the 2000 preconcentrator (FIGURE 2). Currently available inlets include:

- 2016CM 16-Position Tower Canister/Bag Autosampler
- 2016BCM 16-Position Benchtop Canister/Bag Autosampler
- 2016LM 16-Position Tower Loop-Injection Autosampler
- 2016BLM 16-Position Benchtop Loop-Injection Autosampler
- 2001SSI Single Canister Sample Inlet
- TD16A 16-Position Thermal Desorber

Two of these inlets can be connected to the 2000 preconcentrator simultaneously and se-

lected through software. Therefore, a system can have both an ambient air inlet and a source level loop-injection inlet to run both sample types without replumbing when changing back and forth. In fact, it is possible to load up both autosamplers and switch from one to the other automatically. In both cases, benchtop versions are usually preferred only when space is critical (mobile lab) or when the maximum sample number to be run unattended will be low.

## **POLAR AND NON-POLAR VOC'S AT PPT - PPB LEVELS**

Three stage preconcentrations techniques utilizing this configuration have been described previously (Automated 2-Dimensional Chromatography and Microscale Purge and Trap (1)). MP&T, or Microscale Purge and Trap has been found to allow the analysis of all polar and non-polar VOC's tested thus far. With MP&T, the VOC's, H<sub>2</sub>O, and CO<sub>2</sub> are all initially concentrated on the glass beads in the first stage. Up to a 1000cc sample volume can be preconcentrated resulting in detection limits of 5-20ppt on some of the newer high performance quadrupole GC/MS systems (FIGURES 3, 4, & 5). Due to the low affinity of the VOC's on glass beads at room temperature, these VOC's can be transferred out of the first stage by desorbing at room temperature. Most of the water is therefore left behind, just as most of the water remains in the sparge vessel when performing Purge & Trap on water samples. Retrapping the VOC's on the tenax trap at reduced temperatures allows the CO<sub>2</sub> to pass through while retaining even the lightest TO14 target analytes. Subsequent on-column focusing and desorption yields maximum detection limits for the entire range of VOC's. Since CO<sub>2</sub> is mostly removed, cryogenic cooling of the GC oven is not required to increase the separation of the otherwise massive CO<sub>2</sub> peak and the first eluting TO14 compounds. This results in a tremendous savings of liquid nitrogen.

## **TRACE VOC'S IN HIGH CO<sub>2</sub> MATRICES**

When it's necessary to perform preconcentrations to detect VOC's at the low ppb level in matrices consisting of 1-50% CO<sub>2</sub> (soil gas, landfill gas, auto exhaust, etc.), straight cryogenic trapping on glass beads will not achieve optimum results because the CO<sub>2</sub> will concentrate right along with the sample. Cryogenically preconcentrating 50cc of a sample containing 50% CO<sub>2</sub> would result in 25cc of CO<sub>2</sub> being expanded into the GC/MS at a carrier flow rate of 1-2 mls a minute. The resulting pressure burst will actually expand the CO<sub>2</sub> back into the GC carrier gas regulation devices requiring up to several hours to bring CO<sub>2</sub> backgrounds down to acceptable levels. Using the universal 3-stage configuration, a "High CO<sub>2</sub> Sample" application can be selected which maintains the first trap at 60 deg. C to force initial preconcentration to occur on the tenax trap at reduced temperatures. CO<sub>2</sub> passes through the trap much faster than the targeted VOC's and is further eliminated by flushing the trap with an additional 50-100cc helium. Back-flushing of the tenax trap followed by optional focusing can then be performed.

## **HIGH CONCENTRATION SAMPLES (SOURCE)**

Quantification by GC/Quadrupole MS optimally requires 0.1 to 1000 ng of material to be injected. When sample concentrations reach 1-10,000 ppm, this quantity can be obtained using loop injection volumes of approximately .1- 1cc. In order to keep these high concentrations away from the ambient air portion of the system, a separate 16-position autosampler is available that only flushes the contents of the loop into the preconcentrator (FIGURE 6). Transfer of the typical 0.5cc sample volume through connective transfer lines and fittings into the second trap is performed at 60cc/min resulting in sample residence times in fittings and valves of approximately 0.5 seconds. This isn't enough time for the sample to diffuse into the dead volume regions of connective fittings, so long periods of flushing to regain a clean system become unnecessary. Using a separate autosampler also means that each individual position won't have to be revalidated for cleanliness from source level to ambient level analysis, as would be the case if a single autosampler was used for both. A graph showing reproducibility of the 2016LM Loop-injection Manifold is show in figure 7.

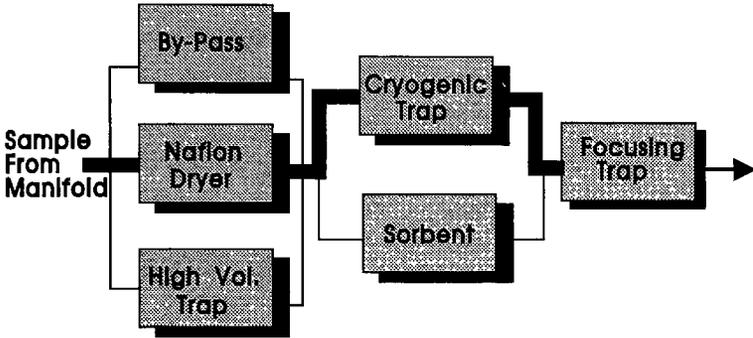
## **SCREENING CANISTERS OF UNKNOWN CONCENTRATION**

To prevent unknowingly exposing the ambient air inlet to high VOC concentrations, canisters of uncertain concentrations can be prescreened using the loop-injection autosampler. Using a single isothermal GC/MS run at 180-200 deg. C, each sample on the autosampler can have an aliquot introduced sequentially onto the GC/MS. Total area counts can then be compared to determine optimum sample volumes for analysis.

## **CONCLUSIONS**

A single preconcentration system has been developed that allows rapid switching between different air matrices. Three different autosamplers are available for TO14 (2016CM), source level (2016LM), and TO1/TO2 thermal desorption (TD16A). Two autosamplers can be interfaced simultaneously permitting software selection of the active manifold. A single trapping configuration also allows for optimizing the preconcentration procedure to accommodate polar and non-polar VOC's in high or low CO<sub>2</sub>/H<sub>2</sub>O matrices. Menu-driven software is used to select the preconcentration procedure based on the user selected application. Default parameters are provided which can be further optimized based on the GC/MS configuration utilized.

ENTECH 2000 PRECONCENTRATOR  
BLOCK DIAGRAM



Classical Method TO14 Pathway

Fig 1

UNIVERSAL INLET SYSTEM  
USING 1 PRECONCENTRATOR  
WITH SEPARATE AUTOSAMPLER

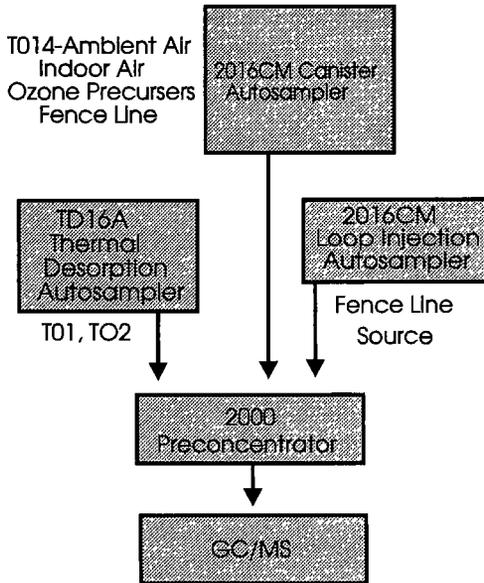


Fig 2

Acquired : Sat Mar 10 93 03:55:41 PM using AcqMethod /chem/airtox1.1.0  
 Instrument : HP5972  
 Sample Name :  
 Misc Info :  
 Vial Number : 31

FIGURE 3 - Reconstructed Ion Chromatogram of a 0.2ppb TO14 standard. Microscale Purge and Trap water/CO2 management was used allowing analysis of both polar and non-polar VOC'S

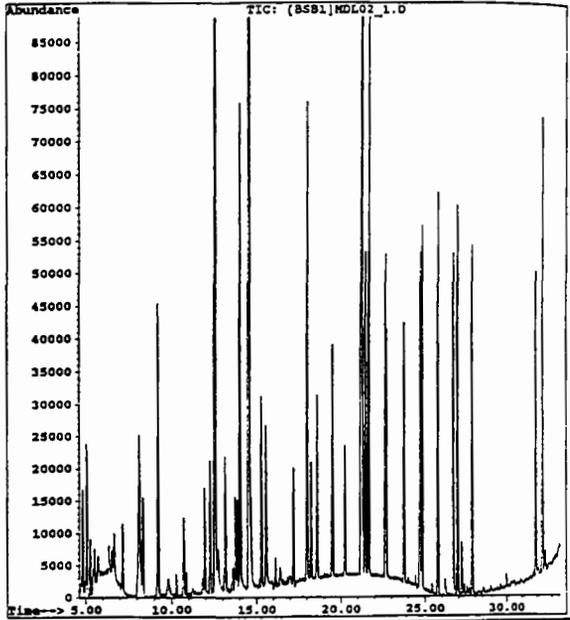
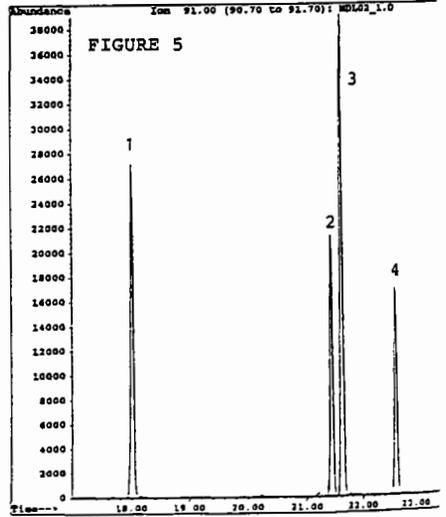
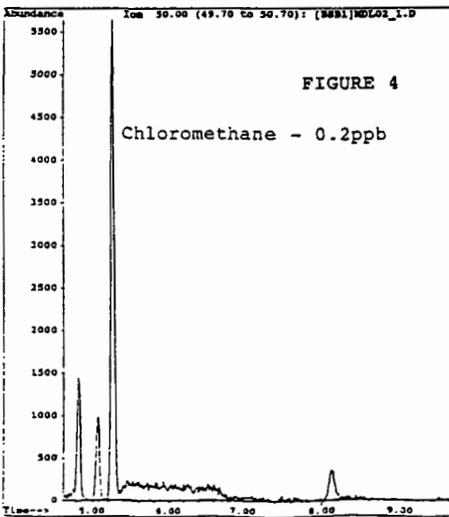


FIGURE 4 - Selected Ion Chromatogram (m/z 50) of chloromethane at 0.2 ppb.

FIGURE 5 - m/z 91 Selected Ion Chromatogram showing toluene (1), ethylbenzene(2), m+p-xylene(3) and o-xylene(4) at 0.2ppb.



# 2016LM LOOP INJECTION AUTOSAMPLER

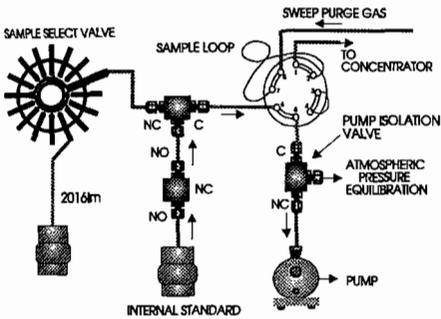


FIG 6

# LOOP INJECTION DATA

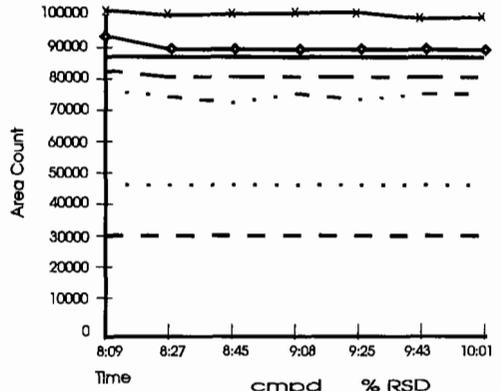
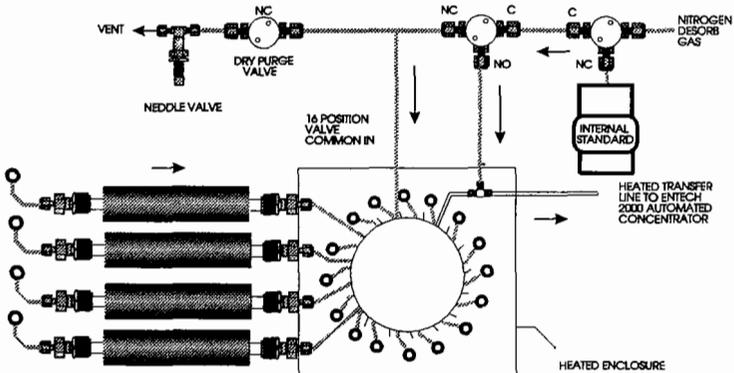


FIG 7

Symbol	Compound	% RSD
--- (dashed)	AN	1.88
... (dotted)	MMA	1.61
—◇— (solid with diamond)	4VCH	1.93
— (solid)	EB	1.33
—·— (solid with dots)	STY	1.93
—x— (solid with x)	CUM	1.82
- - - (long dashed)	AMS	1.76

# TD16A DIAGRAM



## TUBE DESORBER OPTIONS FOR TD16A

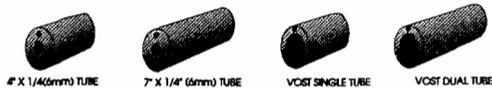


FIG 8

**The Development and Evaluation of a Transportable  
Fast Gas Chromatograph for the Monitoring  
of Organic Vapors in Air.**

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**ABSTRACT**

Gas Chromatography has the potential to be a real-time or near real-time monitoring method for organics in air. A transportable fast GC with FID/ECD and PID/ECD configurations has been developed. Preliminary evaluation has shown that all design features and improvements of the instrument worked successful.

**INTRODUCTION**

Gas chromatography is often used for ambient air monitoring. However, its usefulness for this purpose can be limited by retention times of several minutes and by the limits of detection. This has heightened the need for the development of high speed monitoring systems. Applications requiring real-time or near real-time capabilities include emergency response activities, stationary-source plume tracking, and fence line monitoring. In order to meet this requirement, a fast GC system has been developed and evaluated (1-5).

The most important component of the fast GC is the high speed inlet system. The electrically heated, nitrogen cooled inlet system produces significantly narrower injection bands than can be accomplished using alternate technologies. The retention times of components of mixtures are thereby reduced to just few seconds. This is 50 to 100 times shorter than can be otherwise accomplished. Although part-per-billion (ppb) level limits of detection (LOD) are achieved using this system with only a 1.0 cm<sup>3</sup> sample volume, collection and preconcentration of contaminants from relatively large volumes of air is possible.

Recently, the design and evaluation of a laboratory-based fast GC has been reported. These reports included information on instrument design and the LODs for 41 EPA target analytes (4). The applicability of fast GC was also tested for the analysis of components of complex mixtures of organic vapors in ambient air (5). In that study, mixtures of up to 34 components were separated in less than 100 second, and up to 1000 effective theoretical plates per seconds was achieved.

Additional requirements such as portability have prompted the need to incorporate new improvements into the fast GC. These efforts have resulted in the development of a transportable version of the fast GC. This paper presents the design, development and preliminary evaluation of the transportable fast-GC.

## **METHODS**

The goal of the design of the transportable fast-GC is to maintain performance and improve transportability and the logistics of operation. To reach this goal, several significant improvements were made when compared to the laboratory-based fast GC. The transportable fast GC was built by adding a high-efficiency cold trap inlet, a high speed electrometer, and a laptop personal computer based data system to an HNU Systems model 311 transportable Gas Chromatograph. A Schematic diagram of the transportable fast GC is presented in Figure 1. The following is a discussion of the changes made on the transportable fast GC compared to the laboratory-based fast GC.

### **Inlet System**

As shown in Figure 1, the inlet system for the transportable fast GC includes a six port valve which is mounted inside of the oven. This allows the sample loop to be thermostated without the need for an additional valve oven. An injector port is also mounted on the top of the oven for injection of gas or liquid samples via syringe. The outlet of the injector was connected to a 50 cm long deactivated fused silica buffer column which is used as a transfer line that carried the sample to the cold trap. Since the sample is actually injected by the heating

of the cold trap, the presence of dead volume in the transfer line does not have an adverse effect on instrument resolution.

The cold trap was fashioned from Monel 400 capillary tubing which was enclosed in a small Teflon chamber and cooled by a flow of cold nitrogen gas. For the laboratory fast GC system, the inlet system was built outside of the oven. The sample was injected through the six port valve to the buffer chamber, and then to the cold trap chamber, and then condensed inside the cold trap.

In the laboratory system the buffer chamber/cold trap chamber assembly was made of aluminum, Teflon and copper, and had to be heated to about 75 °C (depend on sample boiling points) to prevent sample condensation in that area. Also, at each end of the cold trap chamber, the trap tubing was clamped between two copper blocks which served as electrical contacts during the heating cycle. The copper blocks were heated to 100 °C with 150 W heating cartridges to prevent sample condensation outside the cold trap.

Comparing these two systems, it is clear to see that the inlet system in the transportable fast GC system is not only a factor of about five smaller, but also far more efficient, simpler and more reliable than the laboratory system.

### **Cooling System**

The basic problem with the laboratory fast GC cooling system was that it was big, immobile, and inefficient. The design of the

transportable fast GC optimized and minimized the use of liquid nitrogen.

In the old cooling system the liquid nitrogen was stored in a 5 L wide mouth Dewar. The nitrogen gas was cooled by running it through a coil of copper tubing immersed in liquid nitrogen, and sprayed into the Teflon cold trap chamber. The trap temperature was controlled by adjusting the nitrogen pressure and was monitored with a thermocouple.

For the transportable fast GC cooling system, the trap temperature can be cooled from room temperature to  $-100\text{ }^{\circ}\text{C}$  in 15 minutes. Ten liters of liquid nitrogen will last at least 8 hours, and as long as 16 hours, of operation. The trap temperature was controlled by a temperature controller and could be stable at setting temperature with  $\pm 1\text{ }^{\circ}\text{C}$  without adjustment.

For the old system, cooling down the trap temperature from room temperature to  $-100\text{ }^{\circ}\text{C}$  took at least 45 minutes. Five liters of liquid nitrogen lasted at most for 3 hours, with the use of large amounts of compressed nitrogen gas from the gas cylinder.

Thus, the new design resulted in a size and supply use rate reduction of an order of magnitude, and a very high degree of improvement in reliability and accuracy of cooling.

#### **Gas Supply System**

For the transportable fast GC system, the gas supplies such as hydrogen, helium, and argon with 5% methane were supplied in small rechargeable cylinders which mounted in the lid of the GC. The refilled gas cylinder could operate at 30 ml/min as carrier gas for at least 16 hours. A small air pump was built on the instrument which could produce a flow rate of 30 ml/min for use with a flame ionization detector. These replaced two 1A cylinders. The installation of the air pump in the system was one of the ways to minimize the size of the instrument. It also represented an improvement in ease of instrument use.

#### **Electrometer System**

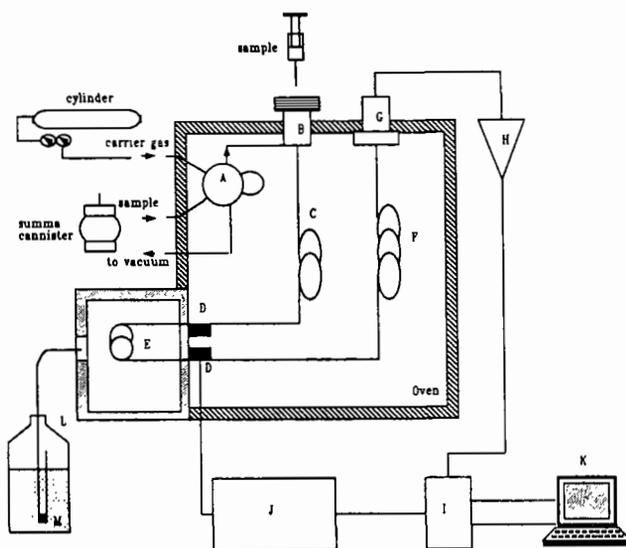
The high speed electrometer-amplifiers with a response time of 5 ms were build for both FID and ECD in transportable fast GC system. These were developed specifically for this application. A single electrometer board was used for both detectors. This board replaced two free-standing electrometer modules that were used on the laboratory instrument. This reduced the size of the electrometer/amplifiers for the two detectors by at least an order of magnitude.

#### **Data Collection**

For the transportable fast GC system, data were collected using an 80386-SX laptop computer equipped with 120 MB hard disk, 8 mb of RAM and an A/D board. The use of a computer with 8 mb of RAM allowed all software and data from an individual chromatographic run to be loaded into RAM disks, thus reducing the data analysis time.

For the preliminary studies being performed on the transportable fast GC, the system was equipped with both a standard HNU flame ionization detector (FID) and an ECD. An HNU Systems-Nordien ECD was used which had a cell volume of 90 microliters. An alternate

configuration of the system that has been used was a photo ionization detector (PID) and the ECD. The PID is an HNU low-volume cell detector (40 microliters). A 30 meter, 0.25-mm i.d., 0.1-um bonded methyl silicone stationary phase capillary column (Quadrex) was used for these tests. Hydrogen was used as the carrier gas for the PID and FID, operated at average linear velocities of 60 cm/sec. Make-up gas for the PID was used at a flow rate of 65 ml/min. The oven temperature was 100 °C.



**Figure 1. Schematic of the transportable fast GC system.**

(A) Six-port rotary valve; (B) Injector; (C) Buffer column; (D) Heated copper electrodes; (E) Cold trap and chamber; (F) Capillary column; (G) Detector; (H) Fast electrometer; (I) A/D and D/A converter; (J) Capacitor discharge power supply; (K) Laptop computer; (L) Liquid nitrogen Dewar; (M) Heater.

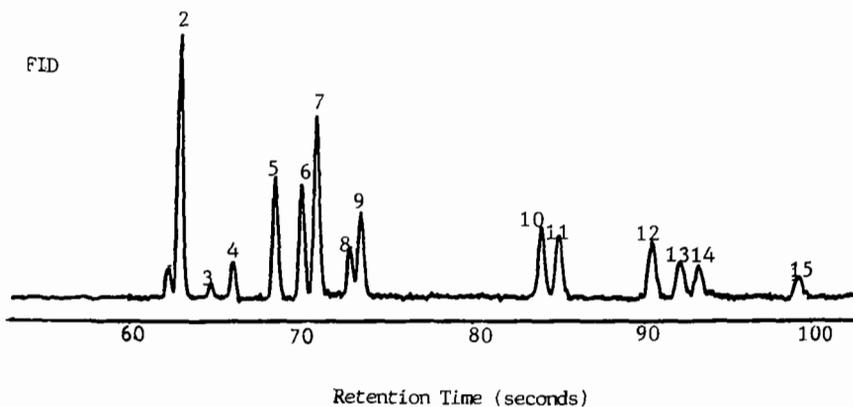
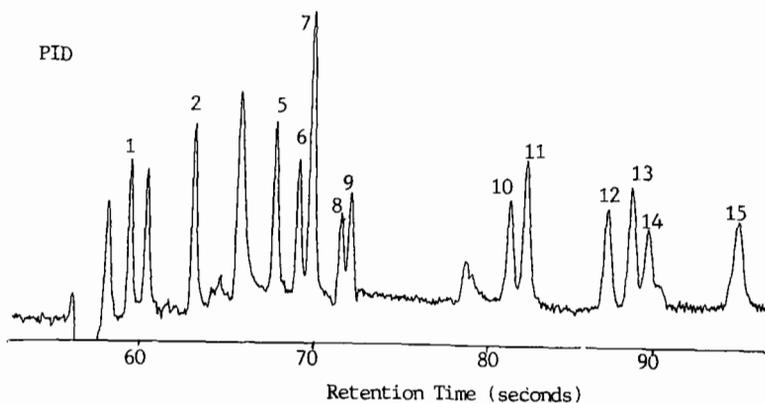


Figure 2. Chromatogram of fifteen-component mixture. The peaks identities are: 1. Benzene(PID only); 2. Toluene; 3. 1,2-Dibromomethane; 4. Tetrachloroethene; 5. Chlorobenzene; 6. Ethylbenzene; 7.m,p-xylene; 8. Styrene; 9. o-Xylene; 10. 4-Ethyl toluene; 11. 1,3,5-Trimethylbenzene, 12. 1,2,4,-Trimethylbenzene, 13. Benzyl chloride, 14. m,p-Dichlorobenzene; 15. o-Dichlorobenzene.

## RESULTS AND DISCUSSION

Figure 2 presents the chromatograms of a fifteen-component mixture of organic vapors in air analyzed with the laboratory fast GC/FID (lower tracing) and the transportable fast GC/PID (upper tracing). As can be seen from these two chromatograms, the transportable fast GC/PID demonstrated similar performance as the laboratory fast GC/FID for this type of mixture.

However, the PID has evidenced two difficulties as a potential substitute for the FID. A negative peak is obtained in a retention time where there may be interferences with the analysis of analytes eluting just before benzene. This is not observed with the FID. The second problem is that detectable background contaminants in the system accumulate with time in the trap. These contaminants are reinjected in the column and interfere with analytes that coelute with them. In order to solve this problem, the trap must be cleaned just before introducing the sample. This strategy represents a ten second delay in the analysis of the sample.

## CONCLUSIONS

In this study, the applicability of the transportable fast GC with the PID/ECD configuration was tested for the analysis of components of a complex mixture of organic vapors in ambient air. The separation of these analytes correlate well with separation obtained with the laboratory fast-GC, but in a more efficient and convenient way.

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## A CRYOGENLESS AUTOGC SYSTEM FOR ENHANCED OZONE MONITORING USING A SIMPLIFIED, SINGLE DETECTOR APPROACH

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### ABSTRACT

A network of real-time autoGCs for C2-C10 hydrocarbon analysis will be implemented over the next 5 years to better correlate levels of ozone and C2-C10 "ozone precursors" in non-attainment areas. These instruments will be operated by state, county, and city agencies with limited personnel and little or no previous exposure to high performance gas chromatography. To insure the collection of meaningful data, it will be necessary to reduce the maintenance requirements and make these systems as reliable and simple to operate as possible.

A system is described that simplifies the cryogenless preconcentration and analysis of the C2-C10 "ozone precursor" hydrocarbons. The incorporation of a dual sorbent trapping system reduces sample moisture without the negative effects of using Nafion dryers. In addition, the two stage trapping procedure eliminates the need for electronic cooling devices that can add cost and complexity to realtime preconcentrators. Cryogen usage in the GC oven has been eliminated by using a multicolumn configuration that optimizes separation of the C2-C10 hydrocarbon fraction at above ambient starting temperatures. A new single detector configuration is also investigated which could greatly simplify the analysis compared to multicolumn/multidetector approaches. Single detector compatibility would also permit laboratory-based GC/MS conformations to be performed using the same chromatographic configuration. The system can operate for weeks without attention, and can down load information into an Excel Data base for ease of reporting. Both data retrieval and system operation can be done remotely using modem communication through a windows operating environment.

### INTRODUCTION

Volatile Organic Compounds are generally regarded as those having a vapor pressure of at least 0.1mm Hg at 25 deg. C. In order to analyze this fraction in ambient air, several other chemical and physical properties must be evaluated before selecting the best possible analytical method. These properties include boiling point, polarity, polarizability (in the presence of a localized charge), reactivity, degrees of freedom ( to assess tendencies to adsorb irreversibly), and 3-dimensional structure. Some VOC's are relatively stable and can be subjected to harsher conditions during sample preconcentration before performing a GC/FID or GC/MS analysis. These compounds can be trapped on chemical sorbents, even those partially oxidized by O<sub>3</sub> and NO<sub>x</sub> exposure, and then recovered at temperatures up to 300 deg. C or higher. On the other side of the spectrum lie compounds that must be sampled, concentrated and analyzed by the gentlest conditions possible as in EPA Method TO3 (direct trapping onto a glass bead trap at -180 deg.

C). In general, all but the most reactive or highly polar VOCs can be sampled and analyzed using compromising methodology such as EPA Method TO14.

Most unsubstituted hydrocarbons and chlorinated hydrocarbons fall under the classification of relatively stable VOC's. These compounds are less affected by partially oxidized sorbents and higher desorption temperatures and may therefore be concentrated successfully without the use of cryogenics or expensive cooling apparatus. Accomplishing this in practice, however, may require multidimensional trapping followed by multidimensional chromatographic separation to accommodate the vast boiling point differences of C2-C12 hydrocarbons. A description of a system that accomplishes this follows.

### **ANALYTICAL TECHNIQUE**

Ambient temperature preconcentration of C2-C12 hydrocarbons followed by capillary chromatography requires at least 2 sorbent trapping stages. The purpose of the first stage is to supply enough sorbent to keep the C2 hydrocarbons from breaking through the trap before the end of the trapping procedure and final trap flush. This requires a fairly wide bore trap with a length considerably longer than classical traps. Since desorption of the first trap can occur with a relatively small back-flush volume (10-30cc), a much narrower secondary trap can be used to further concentrate the sample before injection onto a capillary column for separation and analysis. Rapid injection off the second trap will insure that narrow peaks are obtained in the chromatogram.

As there is a vast difference in boiling points between C2 and C10 hydrocarbons, no one column can currently separate the entire range without the use of cryogenic cooling. Therefore two columns become necessary; one to resolve the light ends and one for the heavier hydrocarbons. These can be arranged in parallel or in series using either pressure diversion or rotary valve flow switching. Series operation is generally favorable as it keeps the heavier fraction off of the column optimized for the light ends which in turn can reduce or eliminate the occurrence of "ghost peaks" (heavy compounds finally eluting from the column that were injected in a previous analysis). Each column is usually configured with its own FID thereby generating two quantitation files that can be merged together in a spread sheet or data base.

### **INSTRUMENTATION**

The Entech 2000 programmable preconcentrator was used to perform the 2-stage cryogenless preconcentration. A 2016BCM 16-position autosampler allowed for preprogrammed selection of a propane standard, retention time standard, blank, and ambient air sample. Primary trapping was done on a 1/4" X 20" multi-bed sorbent trap after which 100cc of helium was used to remove air from the trap before heating (figure 4). Thermal desorption onto a 1/16" x 20" multi-bed trap in the second stage was accomplished with 15-20cc helium under mass flow control. Sample transfer onto each trap was performed with sorbent temperatures ranging from 25-30 deg. C. After preheating the second stage, the GC carrier gas was diverted through the trap at higher than normal flow rates by utilizing Electronic Pressure Control, or EPC (Hewlett-Packard Company, Palo Alto, CA) in order to improve the peak shape of the lighter hydrocarbons. The GC columns were configured as shown in Figure 3. The entire C2-C12 fraction was initially injected onto a

110m DB1 column with the effluent also flowing through a 30m GSQ column (J&W Scientific, Folsom, CA ). After the C2-C3 fraction had been delivered onto the GSQ column, GC flow was diverted directly to the FID thereby isolating the GSQ column. The C4-C10 compounds were eluted by slowly ramping both the oven temperature and column pressure. After a short bakeout, the oven temperature was reduced to 50 deg. C and flow was resumed to the GSQ column to elute the C2-C3 fraction.

## DISCUSSION

Quantitative, reproducible trapping of the C2-C10 fraction was tested using a 56 component Ozone Precursor Standard (Alphagaz) diluted down to 5 ppbv (10ppbv for aromatics). To determine the breakthrough volumes for the primary and secondary traps, each was tested separately by holding all other preconcentration parameters constant. Figure 2 shows the response of ethane, ethene, and acetylene relative to the propane response for different sample

**TABLE 1 - RF's RELATIVE TO PROPANE FOR DIFFERENT TRAP 1 SAMPLE VOLUMES**

COMPOUND	200	400	600	800	1000	1500
Ethane	.65	.67	.67	.64	.68	.65
Ethylene	.69	.68	.71	.69	.71	.68
Acetylene	.63	.65	.66	.65	.64	.55

volumes. As expected from previously reported trapping efficiencies (1), the breakthrough volumes using such a large sorbent bed were over 1000 cc for all analytes. Table 2 shows the recovery in trap 2 using different trap 1 desorption volumes. Acetylene, in particular, was monitored as it had the lowest breakthrough volume on the first trap. Volumes over 20 cc did show loss of the acetylene in the second stage. However, since recoveries of the C10 fraction did not appear to increase with desorption volumes over 15cc, the minimum breakthrough volume in stage 2 was greater than the volume necessary to recover the target analytes from the primary trap.

Figure 7 shows elution of the C2-C5 hydrocarbons directly to the FID without first delivering the C2-C3 fraction onto the GSQ column. Note that although the C2 and C3 fraction does not resolve into individual species, the overall peak shape of these unretained analytes is extremely good, indicating that desorption out of the 1/16" trap using Electronic Pressure Control occurs very rapidly.

**TABLE 2 - RF'S RELATIVE TO PROPANE FOR DIFFERENT TRAP 1 DESORPTION VOLUMES (CC)**

COMPOUND	15	20	25	30	40
ACETYLENE	.65	.64	.58	42	22
1,3,5-TRIMETHYLBENZENE	3.52	3.56	3.58	3.57	3.58

The C4 hydrocarbons were all baseline resolved on the DB1 column starting at 35 deg. C. However, some of the C5 and C6 analytes did not fully resolve from one another. In addition, bakeout of the DB1 column had to be cut short after elution of C12 compounds in order to cool the oven for elution of the C2-C3 held on the GSQ column before it was time to inject the next sample (1 hour continuous operation). Separations and column cleanup could be maximized using this single detector configuration by performing analyses every 1.5 hours rather than hourly. Otherwise, at the moment the only alternative for hourly analyses is to use the more classical 2 column, 2 detector configuration. The HP Chemstation can easily support simultaneous FID operation.

### CONCLUSIONS

The system described was demonstrated to quantitatively trap the complete list of Ozone Precursors with subsequent injection into a GC/FID. No Nafion dryer was required so partial loss of the C2-C3 fraction was eliminated. Also, the lack of a Nafion dryer is expected to reduce carryover and artifact introduction during routine operation. Allowable trapping volumes were 2-3 times greater than reported elsewhere with an expected improvement on the quantitation reliability in the 0.1-0.5 ppbc range. An on-line 16-position autosampler allows several support gases (Analytical and RT standards, blanks) and field samples to be selected by the system on an unattended bases. Utilization of an Entech 4510 real-time integrating controller allows support gases to be sampled and injected while collecting 2-3 hour integrated samples directly into a canister for subsequent analysis. Hence, 24 hour/day coverage does not need to be sacrificed in order to run standards and blanks daily. All of the 56 Ozone Precursors did not separate from one another using the dual column/ single detector GC configuration tested. Until further investigation proves otherwise, a separate FID detector will need to be allocated to monitor the effluent from each of the 2 columns in order to maximize target analyte separations during 1 hour analyses.

This cryogenless configuration is expected to undergo extensive field testing during the 1993 ozone season. Previously obtained Entech preconcentrators can be easily modified to operate without cryogen due to the modularity of the trapping system.

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Entech/HP Ozone Precursor Analyzer  
3 Modes of Operation

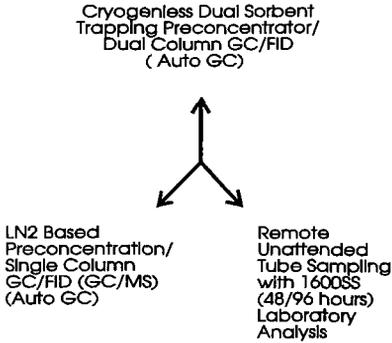


Figure 1

Real Time C2-C10 Ozone Precursor  
Monitoring System

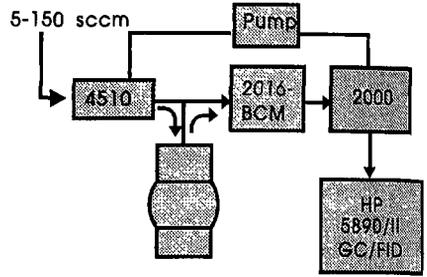


Figure 2

Cryogenless GC Separations

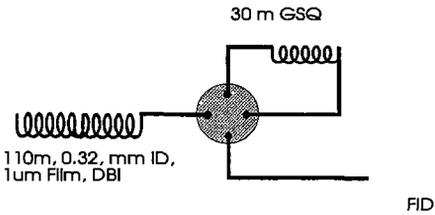


Figure 3

Cryogenless Ozone Precursor  
Trapping

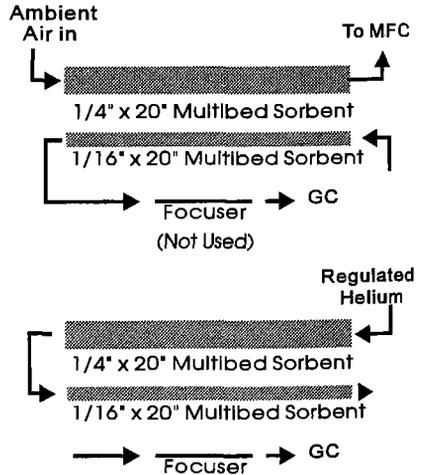


Figure 4

Ozone Precursor  
"Cryogenless" Preconcentration  
Events

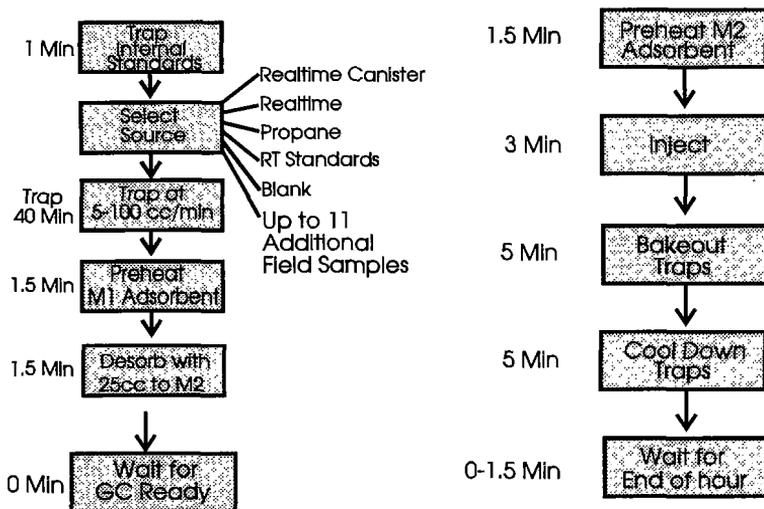


FIGURE 5

3 In 1 Field Sampler, Autosampler  
and Cleaning System

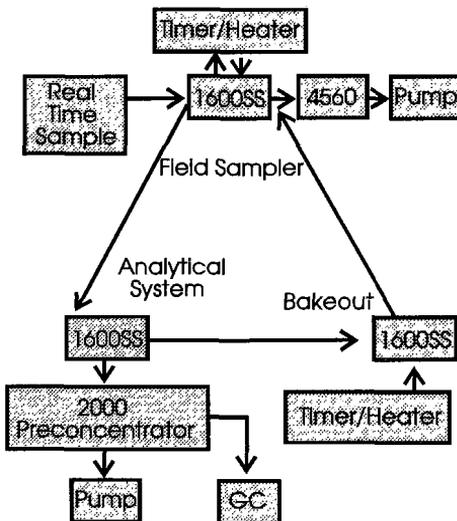


FIGURE 6 - Optional Laboratory analysis of Ozone Precursors using automated sampling onto long sorbent tubes. C2-C10's are all quantitatively trapped and recovered

FIGURE 7 - Dual stage cryogenless preconcentration and injection of C2-C5 mix onto a 110m DB1 column (.32mm ID, 1um Film). Although the C2 and C3 hydrocarbons did not separate at the 35°C starting temperature, they share the same peak width as the C4 and C5 hydrocarbons attesting to the fast rate of splitless injection using EPC.

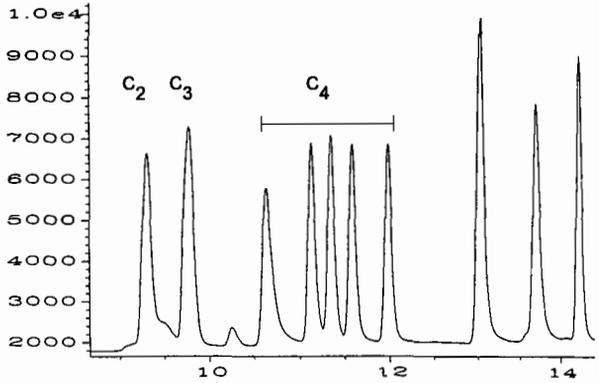


FIGURE 8 - Cryogenless preconcentration, injection and separation of a diluted (5ppbc) alphagaz 56 hydrocarbon standard using two columns and only one FID detector. Initial background contaminants at 38-44 minutes were eliminated after a day of operation (Figure9).

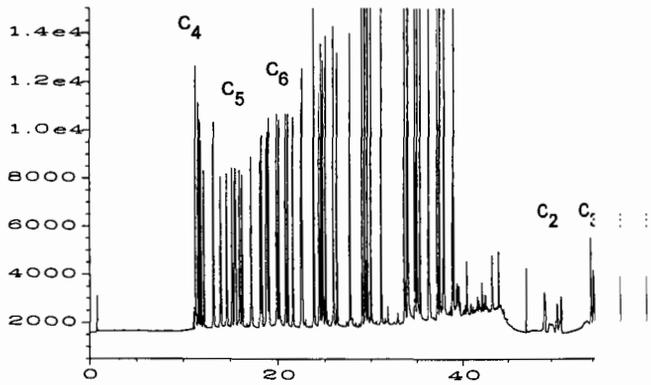
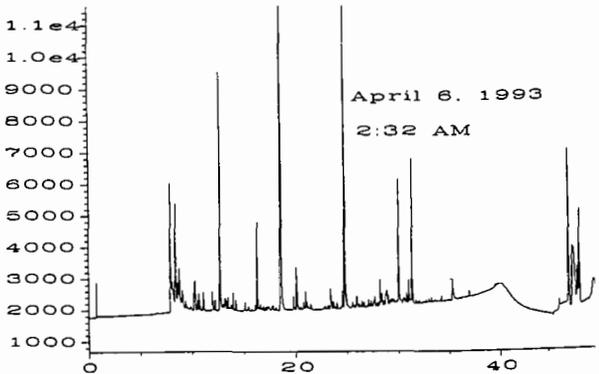


FIGURE 9 - Real time analysis of Los Angeles air at the start of rush hour traffic. C4 compounds and BTEX were in greatest abundance. Estimated detection limits with 800cc concentrated and injected without splitting is about 0.03-0.05ppbc.



# Photoionization Detection of Air Toxics with Microbore Chromatography Columns

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## ABSTRACT

The microchip gas chromatograph has shown enormous potential for on-site identification and quantitation of toxic materials in the environment. Detection limits some 2 to 3 orders of magnitude higher than other portable gas chromatographs, however, limit the utility of the current commercially available unit. The poor detection limit performance has been widely attributed to the use a micro-volume thermal conductivity detector ( $\mu$ TCD). Conventionally, the TCD has been accepted as being grossly less sensitive than detectors such as the flame ionization detector(FID) and, especially for portable GC, the photoionization detector(PID). Other work has suggested that the extremely small size of the microchip TCD results in a much more sensitive TCD, one that is competitive with the FID or PID in terms of sensitivity. This presentation will contrast the relative merits and drawbacks of the TCD and PID in the context of field analytical instruments. The results of a direct head-to-head comparison of the two detectors using a microbore GC column will be presented.

## INTRODUCTION

The current micro gas chromatograph has shown precision and accuracy in the field to a degree unrivaled by other portable chromatographs. The performance is even more impressive when power requirements are considered. The device can provide temperature and operational controls sufficient to provide retention precision to within less than 1% r.s.d. and area reproducibility to within less than 5% r.s.d while drawing approximately 5 to 10 watts. of power from a 12 V power source.

Detection limits from 1 to 3 orders of magnitude higher than other field GC technologies have hindered the realization of the potential in the microchip GC for field analysis. The relatively high detection limits are commonly attributed to the use of an insensitive detector. The available unit currently offers only TCD detection in the form of a micro thermal conductivity detector. There is reason for questioning the seemingly obvious conclusion that the  $\mu$ TCD is the limiting factor in the system's sensitivity; other workers have suggested that miniaturization of a TCD improves its sensitivity. If this is the case other factors may provide the principal limits for the system's sensitivity. Namely, the use of small columns reduces the actual amount of material loaded onto the column and subsequently passing through the detector. The downsizing of the internal volume of the detector may provide advantages with respect to sensitivity. Furthermore, because the instrument is designed for VOC analysis the

detector need not be externally heated. The relatively cooler detector walls that result may provide sensitivity advantages over what is expected by conventional wisdom.

A distinct advantage of the  $\mu$ TCD is its relatively constant response for a wide variety of compounds. While many common detectors respond more strongly to some classes of compounds than others, the  $\mu$ TCD exhibits relatively uniform response characteristics among numerous classes. Relative responses for photoionization detectors vary by approximately an order of magnitude between, for example, aromatic and aliphatic hydrocarbons.<sup>1</sup> Similarly flame ionization detectors show very low response toward perhalogenated compounds.<sup>2</sup> Often detector selectivity can be put to good use; neither the PID nor the FID respond to water, eliminating the difficulty of quantitation in the presence of a large, ubiquitous background peak. Detector selectivity also eases chromatographic resolution requirements in *predetermined* analytical methods. An important disadvantage of relying on selective detectors is that the methods tend to be brittle, applying only to a given set of analytes in a narrow window of sample types. If the sample matrix, including interfering analytes, changes greatly then the method often must be changed to accommodate new interferences. Secondly, the ability to make semiquantitative estimates in the absence of authentic analyte standards is confounded.

Developments in the application to fast microscale chromatography of well controlled temperature programming and heated injection systems presage the advent of similarly portable instruments for semivolatiles field chromatographs. These developments will necessarily require that the detector be heated to substantially higher temperatures than currently required for VOC instruments. This requirement may make the  $\mu$ TCD unworkable from the standpoint of both sensitivity and longevity as higher operating temperatures will certainly have deleterious effects, although to what extent is uncertain.

Two common detectors generally thought to have sensitivity advantages are the photoionization detector (PID) and the flame ionization detector (FID). Both of these detectors are relatively more expensive to use and maintain than TCD's. Furthermore both the PID and FID show large variations in response over different classes of compounds. Nevertheless, the FID and PID seem to be the most likely alternatives to the TCD. The photoionization detector presents a practical advantage over flame ionization detectors— it does not require an auxiliary supply of fuel or oxidant gas. Consequently a system based on PID detection will be more convenient to transport and operate in the field. The small volume of the  $\mu$ TCD offers the possibility of routinely using serial detectors to provide additional confirmation of analyte identities. As an initial step in looking at the feasibility of alternatives to TCD as the detector in microbore GC we have begun to quantify the tradeoffs involved using photoionization detection with the micro GC.

## EXPERIMENTAL

A commercial micro GC unit was obtained from MTI Analytical Instruments. The unit was equipped with a 4-meter x 0.1 mm i.d. OV-1701 column (df=0.4 $\mu$ ). The detector was the standard MTI micro thermal conductivity detector (internal volume <1 $\mu$ L). The unit was modified by adding a 0.5

meter x 0.1 mm i.d. deactivated fused silica transfer line was attached to the outlet of the  $\mu$ TCD detector using zero dead volume fittings immediately at the  $\mu$ TCD effluent line. This line allowed other detectors to be used in line with the  $\mu$ TCD detector. The  $\mu$ TCD volume was equivalent to less than 1% of the total column length. Helium was used as the carrier gas. The flow rate for the microbore GC column was set to 35 cm/second ( $\approx$ 0.2mL/minute). Thus the residence time in the transfer line was approximately 1.5 seconds.

The transfer line from the micro GC was connected to the detector inlet of a Photovac 10S50 portable GC. The detector response was recorded from the d.c. recorder output on the 10S50 GC. An A/D interface that emulated that found in the micro GC was used to digitized the PID detected chromatograms which were collected using the M2001 software package, designed at the Institute for Environmental Studies to operate the MTI GC for simultaneous 2-dimensional chromatography.<sup>3</sup> The same software was used to record chromatograms as detected by the  $\mu$ TCD. This procedure ensured that both data streams were being treated identically in software.

The  $\mu$ TCD required no optimization or setup other than allowing it to warm up. The principal optimization variable for the PID was makeup gas. UHP grade nitrogen was used as makeup gas for the PID. The PID response to mixtures of normal hydrocarbons in air was evaluated as a function of makeup flow and, under the optimum conditions, that response was compared to the  $\mu$ TCD response.

Gas mixtures were prepared by flash evaporation of neat liquids into a flowing air stream. They were held in Tedlar sample bags for use and fresh mixtures were prepared each day. Samples were introduced into the micro GC using the standard sample loop mechanism in the commercial unit. A minimum of 2 ml of sample was flushed through the sample loop to minimize sample loss and carryover; a 2 ml sample corresponds to about 200 sample line volumes.

## RESULTS AND DISCUSSION

Three closely related aspects of PID and  $\mu$ TCD sensitivity have been briefly addressed— (1) signal to noise ratio for individual chromatograms, (2) peak shape, and (3) detection limits for analytes. The most basic determination is the signal to noise ratio for peaks in a chromatogram. This value is related most specifically to the detector comparison as the two detectors, connected in series, measure the same sample. Comparison of the peak shapes at the two detectors indicates the relative the effect on resolution of the detector system. As detectors rarely have other than deleterious effects on peak shape and resolution, comparison of PID and  $\mu$ TCD indicate the relative damage each causes to the chromatography. Finally, the bottom line in any quantitative analysis system is often “detection limit.” The main question at this point, in gauging the relative performance of the alternative detectors is “does the use of one detector in the overall system offer a performance advantage over the other detector. Consequently the detection limits for the system using each of the detectors were compared for a series of mid- and low-ppbv air samples.

## Signal to Noise Ratio

Figure 1 shows relative response of the photoionization detector and the micro thermal conductivity detector to a sample containing 100 ppmv each of pentane and hexane. While the PID response in Figure 1 is roughly equal to that for the  $\mu$ TCD, the gain setting for the PID was a factor of 100 below the maximum. While the  $\mu$ TCD was operating at maximum sensitivity, the PID was operating well below its maximum sensitivity. Note that the retention times in have been corrected for residence time in the transfer line. The PID apparently is capable of much higher sensitivity than the  $\mu$ TCD. Both traces have the same limiting noise level; so the relative responses of the two detectors would look the same if they were compared on the basis of signal to noise ratio. The source of the noise limitation is an important consideration in extrapolating the results, especially in the projection that the PID may be 100 time more sensitive than the  $\mu$ TCD. If the noise is in the detector response itself or between the detector and the electrometer, then increasing the electrometer gain by a factor of 100 will do nothing to increase analyte detectability; the relative sensitivity of the two detectors will be as illustrated in Figure 1 regardless of the gain setting on the PID electrometer. The source of the limiting noise is currently being investigated.

## Peak Broadening

Another striking feature of the comparison is the peak broadening seen in the PID trace. Figure 2 illustrates the degree of peak broadening seen in the PID result compared with the  $\mu$ TCD result at several makeup gas flow rates. The curve for the  $\mu$ TCD shows the expected (and observed) trend in peak width as a function of adjusted retention time for the column with little or no post column peak broadening. This curve intersects the y-axis, representing an unretained peak, at approximately 250 ms, which is the width of the injection zone. The PID result shows considerably broadened peaks both without makeup gas, as expected, but also with even large flows of makeup gas. Increases in makeup flow improved peak shapes only up to makeup flows of about 10 ml/minute. Subsequent increases in makeup flow rates did not further improve peak shapes. Peak widths for late eluting peaks were comparable for both detectors, but earlier eluting peaks were progressively more distorted by the PID detector. The peak width of the PID detected peaks approached a minimum value of 2 seconds. This is consistent with a response time constant of about 1 second. In other words, an infinitely sharp peak passed through a detector with a 1 second time constant would have a half height width of about 2 seconds. Internal detector volume was eliminated as a source of the peak broadening because continued increases in makeup flow did not further reduce the peak widths. Residence time in the transfer line was too short to contribute so much to the post column broadening. Replacing the PID with a Hewlett Packard flame ionization detector verified that the transfer line was not the source of the broadening. The likely source of the peak broadening in this study was insufficient bandwidth of the Photovac electrometer. In order to accurately represent the sharp peaks eluting from the short 100 $\mu$  columns in the microGC unit, the detector (including the electrometer) must have a time constant below 0.075 seconds. As with signal to noise ratio, further investigation is required to quantify the sensitivity comparison inherent in the detector. A faster electrometer (i.e., larger bandwidth) may mean a higher limiting noise level. A

fundamental, direct, relationship exists between the bandwidth of an amplifier and the magnitude of random noise in the signal. Another way to conceptualize this is to think of a slow electrometer as a low pass noise filter. Thus it is possible that the some of the apparent two order of magnitude sensitivity advantage of the PID may disappear when the faster electrometer is used. Again, as with the signal to noise ratio measurement, much depends on the ultimate source of the noise.

### Detection Limit

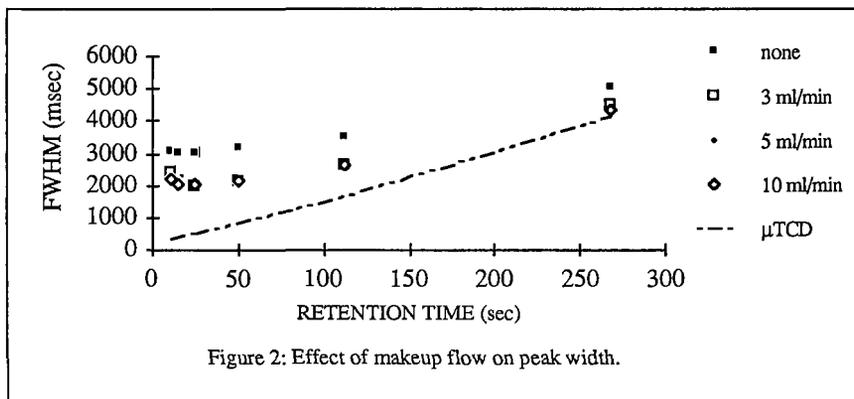
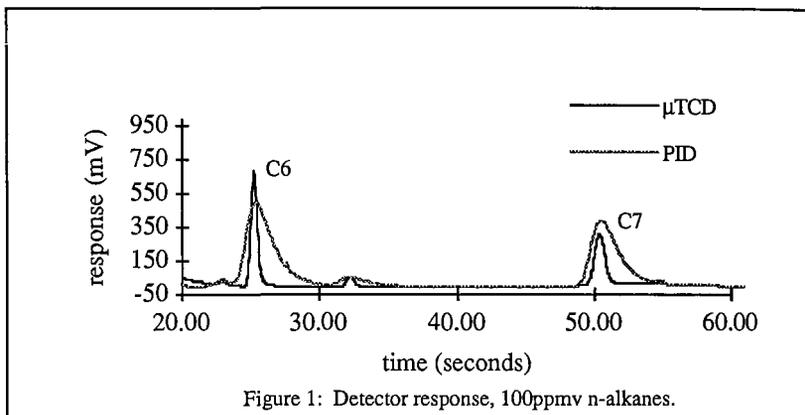
The calibration curve for a set of standard air mixtures containing n-alkanes at concentrations from 1000 ppbv to 50 ppbv are shown in Figure 3. The standard deviation of peak areas for all compounds ranged from about 0.5 mV-s at 50 ppbv to about 2.5 mV-s at 1000 ppbv. On the basis of the standard deviation at 50 ppbv and the calibration curves shown in Figure 3, the detection was estimated at 20 to 50 ppbv for all of these alkanes. Given that the PID is about 10-fold more responsive to benzene than to n-hexane one may expect that the detection limit for benzene would be in the 2-5 ppbv range. The caveats of making such an extrapolation were discussed above and apply here as well. Nevertheless, this is somewhat higher than the extant estimate of 0.1 ppbv benzene detection limit often cited for portable GC's using photoionization detection. Previous workers have determined detection limits for the commercial microGC unit to be about 200 ppbv.

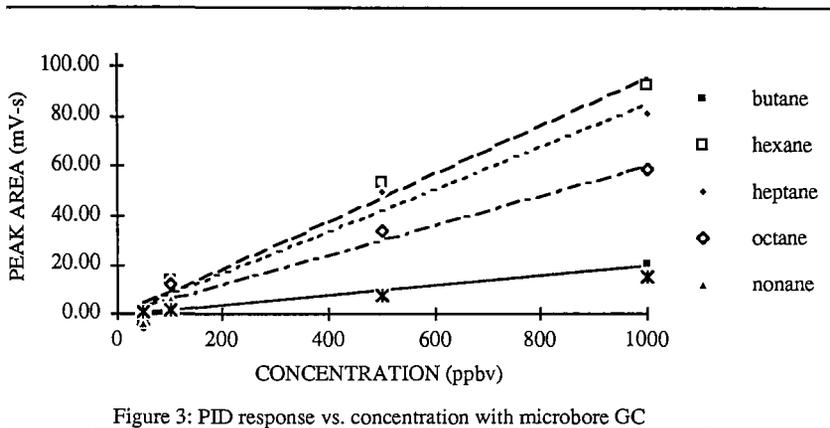
### CONCLUSIONS

On the basis of signal to noise ratio for a single chromatogram, photoionization detection with microbore gas chromatography seems to be approximately 100 time more sensitive than the  $\mu$ TCD. The slow electrometer used here extracted a substantial price in terms of degraded chromatographic resolution. A loss in that sensitivity advantage may be realized with a faster electrometer because of the relationship between higher bandwidths (i.e., faster electrometer) and higher levels of random noise. When the total system was evaluated the advantage in detection limits for the PID over the  $\mu$ TCD was only about a factor of 5 for n-alkanes. For benzene the advantage may be as much as 50 if the extrapolation using the relative response to benzene is to be believed. The PID advantage over the  $\mu$ TCD may not be as phenomenal as it first seemed, though it does seem clear that there is some advantage. Precise quantitation of how much is gained by using a PID with microbore GC must be compared with the costs of operation, maintenance and development of a PID system for the microGC.

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## NEAR REAL-TIME GC ANALYSIS OF VOLATILE ORGANIC COMPOUNDS USING AN ON-LINE MICRO-TRAP

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### ABSTRACT

Micro-traps act as sample pre-concentrators for gas chromatography (GC) that can be used to make repetitive injections every few seconds. A thermal desorption micro-trap is made from a short segment of thin tubing containing an adsorbent or a chromatographic stationary phase. A carrier gas containing the analyte of interest can be introduced into the GC analytical column through the micro-trap which acts as a sample trap. Rapid heating of the micro-trap releases a "concentration pulse" of the analyte that serves as a GC injection similar to that from an injection valve. Micro-traps can be used in various applications such as process stream analysis, fast and multi-input chromatography.

### INTRODUCTION

In recent days, the volatile organic compounds (VOCs) have received much attention as air pollutants and several are listed in the Clean Air Act Amendment of 1990, Title III. The analysis of VOCs is particularly challenging because they are usually present in very low concentration (ppmv to ppbv level). VOCs in gaseous matrices such as stationary stack emissions are analyzed using whole air samples collected either with the Volatile Organic Sampling Train (VOST)<sup>1</sup> or with Tedlar bags using EPA Method 18<sup>2</sup>. Both these approaches attempt to analyze dilute gaseous matrices by concentrating a small amount of analyte from a large volume of gas. While these methods are quite effective in VOC measurements, they can not be used for continuous or near real-time monitoring.

The important feature of any continuous, on-line GC instrumentation is the sample introduction system, that is required to make automatic, reproducible injections. In many chemical industries, process GC is accomplished by the use of sample valves as injectors. Valves can automatically make injections from a sample stream onto a GC column. However, sample valves have certain limitations. Being mechanical devices, they tend to deteriorate during extended operation. Also, sample valves can only handle small volumes of gas, generally between a few  $\mu\text{L}$  and two mL. Injecting a large sample volume causes excessive band broadening and degrades chromatographic resolution. A small sample volume results in reduced sensitivity. As a result, sample streams that are at sub part per million concentration levels can not be effectively analyzed using sampling valves. In many applications, especially in environmental monitoring, low VOC concentrations are encountered and sample valves are found to be inadequate.

Real-time VOC monitoring (at trace levels) using a GC, requires an automated injection device and a sample preconcentrator. The research reported here used an on-line micro-trap to serve the dual purpose of

sample concentration and injection.

#### On-line Micro-trap

An on-line micro-trap was made by packing a short (few cm long) piece of metallic or fused silica tubing with an adsorbent. The sample containing the analyte is introduced into the analytical column through the micro-trap. The analytes are retained in the micro-trap and can be thermally desorbed by electrically heating the micro-trap. When the heating is rapid enough, the desorption generates a concentration pulse that serves as an injection. The different compounds are separated by the column and analyzed by the detector. The mode of operation for continuous monitoring is that injections (or pulses) are made at fixed intervals of time and corresponding to each pulse, a chromatogram is obtained. The advantage of the micro-trap is that it has low thermal mass and can be heated/cooled very rapidly. So, repetitive injection can be made as long as GC separation is completed. The amount of sample trapped in the micro-trap is proportional to the concentration of the stream sampled. Consequently the micro-trap response is proportional to sample stream concentration.

#### EXPERIMENTAL SYSTEM

The experimental system is shown in the Figure 1. The VOC sample stream was generated by entraining the analytes from a diffusion tube onto a flow of nitrogen. The analyte concentration was controlled by changing the diameter and the height of the liquid level in the diffusion capillary. The concentration of the stream was calculated using diffusion equations.

A Hewlett Packard GC (model 5890) equipped with a flame ionization detector (FID) was used in this study. The micro-trap was made by packing 0.5 mm ID stainless steel tubing with different adsorbents. The micro-trap was heated by passing a pulse of electric current (duration 100 to 700 msec) directly through its metal wall. The injections were controlled by an IBM compatible personal computer using the digital output of the analog to digital converter (DASS-PGA, Metrabyte Corp.) and an electronic switch (OACSP, Opto 22, Huntington Beach, CA). The micro-trap was heated at fixed intervals of time. The interval between injections varied between 5 and 300 sec. A computer program written in Quick Basic was used for making injections as well as for data acquisition.

#### RESULTS AND DISCUSSIONS

The operation of the continuous analysis system was demonstrated by continuously monitoring a stream containing ppb<sub>m</sub> levels of hexane, dichloromethane, toluene and ethylbenzene. The injection from the micro trap (referred to as a pulse) was similar to that from an injection port or valve. A series of pulses were generated at one minute intervals. Each pulse produced a four peak chromatogram as shown in Fig. 2. The high sensitivity of the micro-trap is quite obvious, chromatographic separation may be reduced by shorting the pulse interval to 45 seconds or installing microbore columns.

Reproducibility of retention time as well as peak height was very good for the micro-trap and was comparable to that of an injection port. Since the flow through the micro-trap is very compatible to the flow through the column and there is practically no dead volume, the micro-trap produces sharp peaks. Linearity of the calibration curve is also an important consideration for on-line measurements. The amount of sample trapped by the micro-trap is theoretically proportional to the concentration of sample flowing through it. Here we found the calibration curve to be linear in the ppb to ppmv range.

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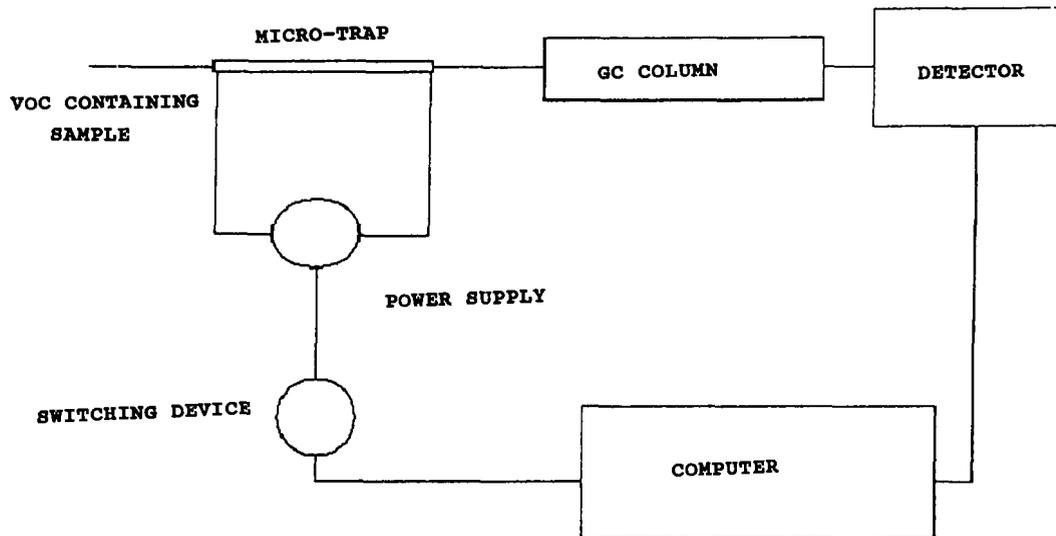


Figure 1. Schematic diagram of the experimental system

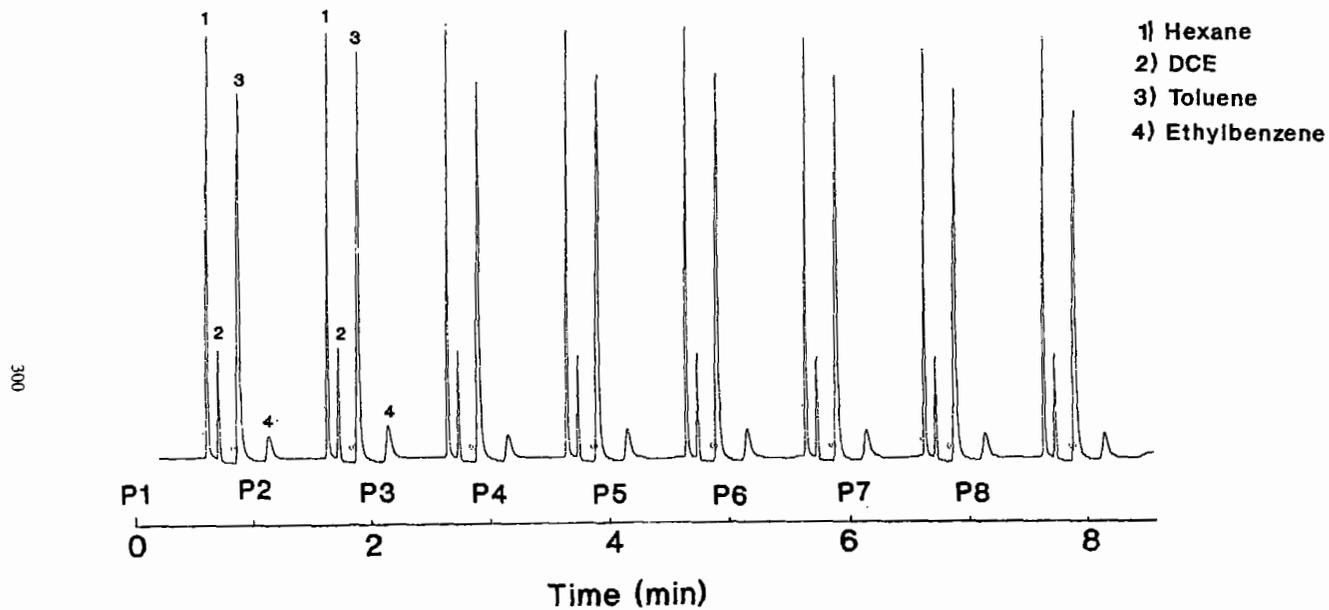


Figure 2. Continuous monitoring of VOCs using the on-line micro-trap.  $P_1, P_2 \dots$  are the different injections corresponding to which chromatograms were obtained.

## THE USE OF ANALYTICAL AND METHOD SURROGATES IN GC/MD ANALYSIS OF WHOLE AIR SAMPLES

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### ABSTRACT

USEPA Compendium Method TO-14 describes the general approach necessary to successfully analyze 40 compounds by either GC/MS or GC/MD. The introduction of automated interfaces which concentrate the air sample prior to introduction into the analytical system provide an opportunity to include additional quality control measures. An analytical surrogate, a compound added to the preconcentration device during sample concentration, can help assess data quality during unattended operation. A method surrogate can be added into the canister sample prior to dilution/analysis to provide an indication of analytical accuracy, including sample dilution and analysis.

Addition of surrogates allows the continual assessment of analytical accuracy and precision during TO-14 analyses. The use of two surrogates introduced at different points within the analytical process help define many potential problems. A method surrogate can be used to assess the effects of sample matrix and handling while the analytical surrogate provides a measure of interface, gas chromatograph, and detector performance.

### INTRODUCTION

The analysis of whole air samples by GC/MS or GC/MD for volatile organics is a well established technique. EPA Compendium Method TO-14 describes sample collection, target compound lists, calibration requirements, and data reduction<sup>1</sup>. However, the use of surrogates as a means of assessing method/analytical accuracy and precision as is common in other EPA methodology is not discussed.

Advances in VOC analytical techniques have increased the need for surrogate addition to improve quality control procedures. An increase in the use of automated interfaces which can analyze up to 16 canister samples in an unattended mode necessitates this additional quality control to insure proper instrument operation and data validity. Instrument problems (such as the column temperature not equilibrated prior to injection, significant changes in carrier or detector gas flows, cryogen outage or failure, and problems with sample loading such as valve failure) which would normally be apparent to an analyst on a real-time basis can be difficult to assess when data are collected in an unattended manner.

The same advances in analytical technology which pose this challenge can be used to solve it using surrogate addition. Several of the commercially available (and privately designed) VOC preconcentration devices provide the capability to add a surrogate onto the trap prior to sample injection. The ability of instrumentation to add such compounds in a very precise manner has been described by Dayton and Bursey<sup>2</sup>. Analytical surrogates can be used to assess proper operation of automated VOC instrumentation.

The assessment of sample handling, storage, and matrix effects are also of interest in evaluating method accuracy and precision. A method surrogate can be added to the canister either prior to or after sample collection to assess (post collection) method accuracy and precision. Method surrogates can be especially valuable when dealing with high concentration samples of unusual matrices (point source samples) which require multiple dilutions and non-routine analytical approaches.

The goal of this study was to develop techniques for and evaluate the addition of analytical and method surrogates during VOC analyses. Acceptable surrogate compounds must be amenable to the GC/MD technique without interfering with potential GC/MS confirmation analysis.

### EXPERIMENTAL METHODS

The study was divided into four tasks: surrogate compound identification, analytical surrogate addition, method surrogate addition, and evaluation. The following paragraphs describe each of these tasks.

#### Surrogate Compound Identification

The search for viable surrogate compounds was first narrowed to the volatility range of the target compounds

(C2 - C12) and organic compounds which respond on multiple detectors (FID, PID, ELCD, OR ECD). It was desirable that the surrogate chromatographically separate from target analytes as well as any compounds routinely observed in ambient air samples. Compound stability was also a concern. The compounds chosen for evaluation based upon these criteria were identified as shown in Table 1.

Each of these compounds was introduced into an evacuated canister and analyzed on a 60m x 0.32mm id DB-1 chromatographic column using an initial column temperature of -50° C for 2 minutes and then ramping 6° C/min. to 175° C. The measured retention time was compared to an ambient air sample and a database of over 200 compounds for potential coelution. Response on each detector was also evaluated.

#### **Analytical Surrogate Addition**

The analytical surrogate was added to the preconcentration device to provide data on sample trapping, desorption, transfer, and detection. Analytical surrogate addition on automated systems necessitates at least one additional valve to introduce surrogate standard into the system in a controlled manner. Figure 1 presents the design of the analytical interface used and how the analytical surrogate was added onto the trap. This addition takes place immediately after sample concentration as a test for cryogen failure or trap blockage. The analytical surrogate (nominally 13 ppbV) was flushed through the interface lines for 90 seconds, 50 mL were loaded onto the trap, the lines were flushed with nitrogen and the system was allowed to reach ambient pressure prior to thermal desorption.

#### **Method Surrogate Addition**

The method surrogate could be introduced into the canister either prior to or after sample collection. If the sample matrix was well defined and the measured concentrations did not vary considerably the method surrogate could easily be added to the canister prior to or post sample collection. If the sample matrix was unknown and the measured concentrations were expected to vary widely the method surrogate could be introduced into the canister post collection. In this manner, the sample matrix could be defined through screening to help identify the correct surrogate and practical spike amounts for each matrix or project.

A fixed loop injection system was used to introduce the method surrogate into the canister. Figure 2 illustrates how the 6 port Valco valve equipped with a 1.1 mL loop made from 1/8" stainless steel tubing was plumbed into a diluent system. A needle valve was used to control method surrogate flow and a rotometer was installed downstream of the loop as a visual check of loop equilibration prior to injection into the canister. The method surrogate, at a nominal concentration of 55 ppmV, was purged through the trap for five seconds. The surrogate standard was closed and after the trap reached ambient pressure (no flow indicated on the rotometer) the valve was rotated to the inject position. The diluent gas flushed the surrogate into the canister.

#### **Evaluation**

The described techniques were evaluated for accuracy, precision, stability, and practical feasibility. Accuracy was assessed by comparing a measured concentration to a theoretical concentration (absolute accuracy) or to the measured standard concentration (relative accuracy). Precision was tested as analytical reproducibility, precision of the analytical surrogate addition and analytical variability, and method variability. Analytical variability was measured as an average relative percent difference between the concentration of the method surrogate in 31 pairs of duplicate analyses. The analytical surrogate data from this same data set represents analytical variability plus analytical surrogate addition variability. Method variability was estimated by collecting the matrix surrogate into seven canisters which were subsequently analyzed. This precision estimate reflects method surrogate addition reproducibility, analytical drift, canister dilution, storage stability, and canister to canister variability.

Method surrogate storage stability was an important factor to evaluate given that the surrogate was introduced into the canister and stored varying amounts of time prior to analysis. The storage stability was tested by measuring compound concentration in eight canisters which were stored up to 24 days prior to analysis. The practical applications for surrogates in ambient and point source samples was tested for precision and accuracy to verify the usefulness of these techniques in actual samples. The results of these evaluations are presented below.

## **RESULTS AND DISCUSSION**

The two compounds which best suited all the requirements for surrogates on the DB-1 analytical column were 1,4-difluorobenzene and 4-fluorotoluene. 4-Fluorotoluene was subsequently selected as analytical surrogate with 1,4-difluorobenzene as a method surrogate for ambient air sample analyses. In this arrangement, 1,4-difluorobenzene could also be used as an internal standard for subsequent GC/MS confirmation analyses in accordance with existing and proposed methodology.

Relative percent accuracy of the analytical surrogate was determined by comparing response of the surrogate in humidified air standards containing 15 - 45 volatile organics (n = 192) to the surrogate response in the appropriate daily method blank. This approach is used for sample recovery and compensates for any slight changes in detector drift over time. A mean relative accuracy (recovery) was thus calculated to be 95%.

The total variability associated with the analytical surrogate (analytical variability plus surrogate addition variability) was 5.7%. This relative standard deviation was obtained from standards which were analyzed over a five day period (n = 39). Analytical variability was estimated at 2.7% based upon the average relative percent difference of 31 pairs of analytical duplicates. Therefore, the hardware and methodology used to introduce the analytical surrogate into the system has less than 5% variability.

The analytical surrogate was further evaluated on two different analytical systems over two days using ambient air samples. The samples used in the evaluation were ambient air samples collected near multiple industrial point sources located in urban settings. The results shown in Table 2 reflect that both systems show a mean relative accuracy (sample surrogate AC/method blank surrogate AC) to be between 98 - 104% and precision (relative standard deviation of the sample surrogate AC) to be less than 8%.

The method surrogate precision (relative standard deviation) was measured to be 1.0% based upon the analysis of seven replicate standards. The absolute accuracy ( $100 \times \frac{\text{measured concentration} - \text{theoretical concentration}}{\text{theoretical concentration}}$ ) of method surrogate addition was + or - 7% based upon the mean measured concentration from the seven replicates. Method surrogate stability data are provided in Table 3 and show no discernable difference between the mean concentration measured over the study period. Therefore, the method surrogate is considered stable from the time introduced into the canister through final analysis (at least 24 days).

Method surrogate capability was further tested using synthetic mixtures (n = 192) described in the analytical surrogate discussion and various point source assessment projects. The method surrogate from the synthetic mixtures had a mean recovery of 115% when compared to the mean measured concentration of the surrogate standard and a relative standard deviation of 14%. Method surrogates were utilized on two projects where high level point source samples were collected and analyzed. One set of samples was characterized by a complex C1 - C7 hydrocarbon mixture with concentrations ranging from 50 ppmV up to 400,000 ppmV. The samples were collected in canisters and tedlar bags. After characterizing the sample matrix, c-2-butene was identified as an appropriate method surrogate due to its retention time and similarity to sample constituents. A method surrogate (12390 ppmV) was prepared and injected into the sample containers after screening the sample matrix. After multiple sample dilutions, the mean method surrogate recovery (measured concentration/theoretical spike concentration) was 105% with a standard deviation of 20.9 (RSD = 19.9%). A large portion of this variability centered around one sample, however, and may represent matrix effects.

## CONCLUSIONS

The use of surrogates can be very important in insuring valid sample handling and analysis when automated instrumentation is employed. This study has shown that surrogates can be reproducibly added to samples prior to analysis and at the time of analysis. Two fluorinated compounds, 4-fluorotoluene and 1,4-difluorobenzene, are viable analytical and method surrogates for GC/MD analyses of volatile organics in ambient air. These surrogate data can be used to validate sample dilutions and proper instrument performance in a timely manner.

The chosen surrogate compounds work well with most ambient samples but may not be feasible for all point source samples. In such instances, the surrogates must be custom tailored to a specific project or matrix to be representative of the target compounds and to avoid chromatographic coelution.

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Figure 1. Schematic of Automated Analytical System.

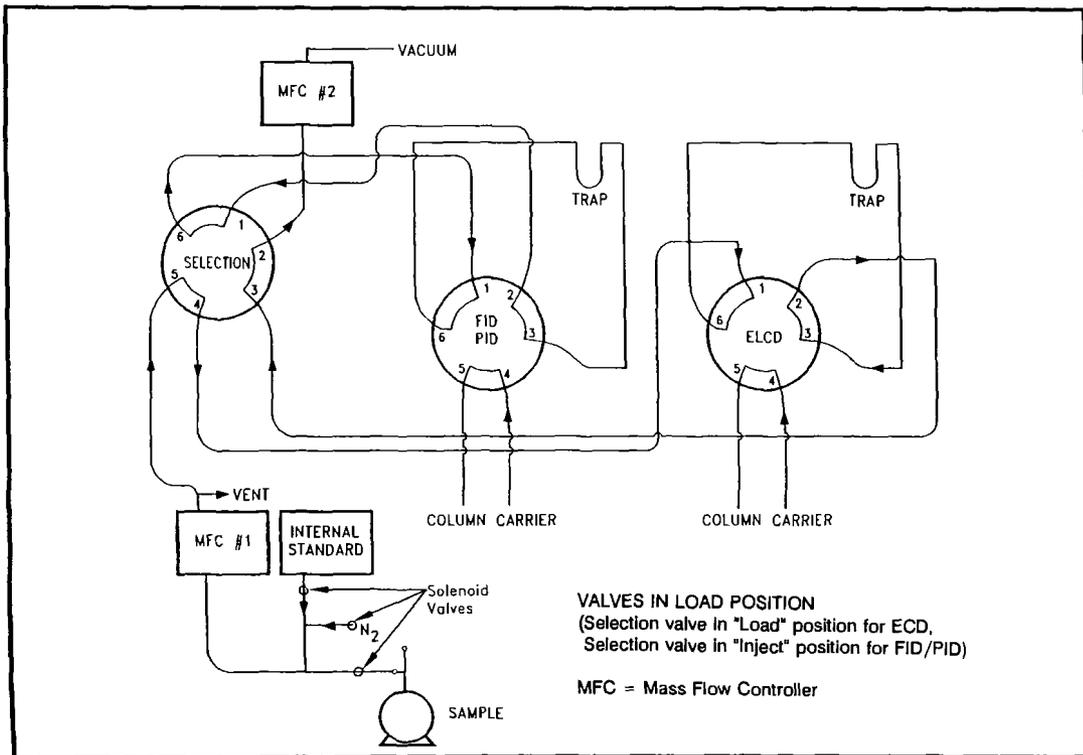
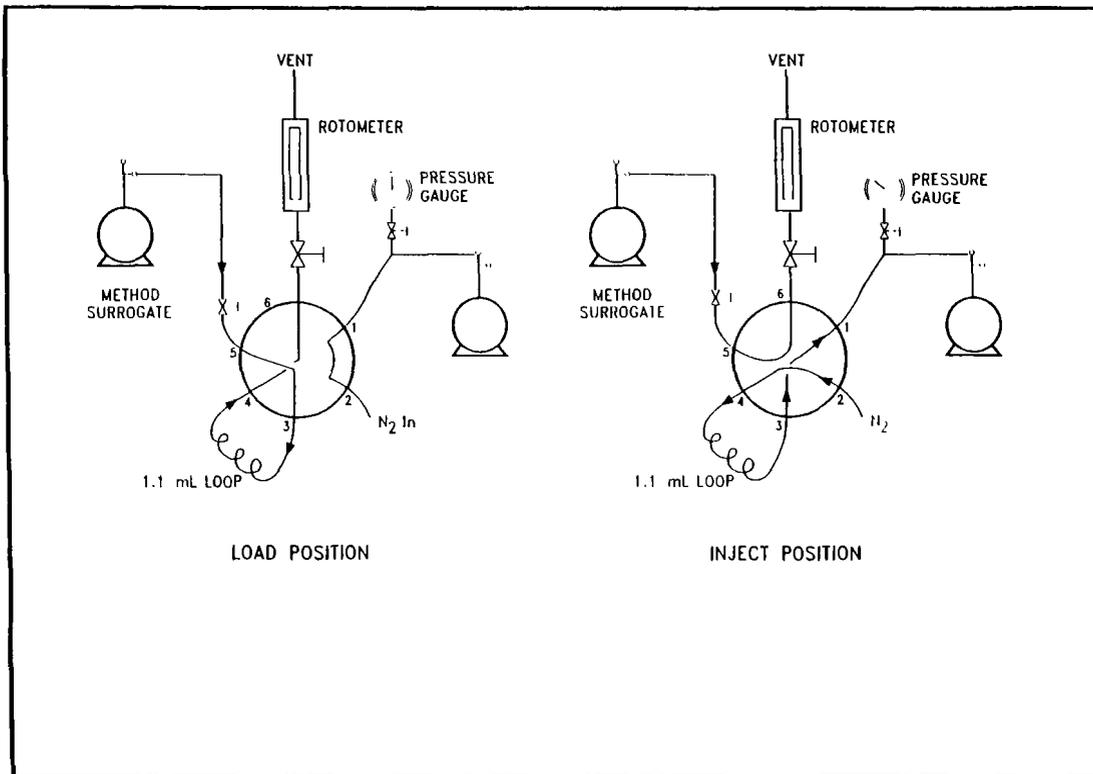


Figure 2. Schematic of Sample Dilution Device.



**Table 1. List of Potential Surrogates for VOC Analyses.**

Methyl iodide	1,4-Difluorobenzene
Methyl formate	Trifluoromethane
Dimethyl ether	3-Chloropropene
Allene	2-Bromopropane
1-Fluoropentane	Bromofluorobenzene
4-Fluorotoluene	Chlorobenzene-d5

**Table 2. Precision and Relative Accuracy of Analytical Surrogate in Ambient Air Samples.**

	ANALYTICAL SYSTEM 1		ANALYTICAL SYSTEM 2	
	Day 1 <sup>a</sup>	Day 2	Day 1	Day 2
Method Blank (Area Count)	7871	11641	13560	13953
Sample 1 (Area Count)	7669	11756	13898	13821
Sample 2 (Area Count)	7997	11928	12131	14937
Sample 3 (Area Count)	8006	11843	13837	13052
Sample 4 (Area Count)	8068	12401	13816	13555
Sample 5 (Area Count)	7921	12445	13355	13639
Sample 6 (Area Count)	7987	12159	13070	13357
Sample 7 (Area Count)	9583	12060	12881	
Sample 8 (Area Count)		11564	14010	
Mean Response (Area Count)	8176	12020	13374	13827
Standard Deviation (Area Count)	634	308	650	648
Rel. Std. Dev. (Mean Sample AC/blank AC)	7.8%	2.6%	4.9%	4.7%
Mean Recovery	104%	103%	98.6%	98.4%

<sup>a</sup> Day 1, system 1 response showed higher than expected variability so the load time/volume was increased to produce better precision.

**Table 3. Method Surrogate (1,4-difluorobenzene) Stability Data.**

Day <sup>a</sup>	Number of Observations	Mean (ppbV)	Std. Dev. (ppbV)	Rel. Std. Dev. (%)
1	8	19.3	0.644	3.3
7	4	18.4	2.10	11.4
14	4	19.1	0.755	3.9
24	4	19.1	0.882	4.6

<sup>a</sup> Elapsed time (days) between surrogate spiking and analysis.

## MOISTURE MANAGEMENT TECHNIQUES APPLICABLE TO WHOLE AIR SAMPLES ANALYZED BY METHOD TO-14, II; GC/MS CONSIDERATIONS

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### ABSTRACT

Analysis of polar organic compounds collected in canisters using US EPA Compendium Method TO-14 is of interest to a number of industries and agencies. However, it is commonly known that moisture in the sample can interfere with the analysis. Most water removal techniques also remove low molecular weight oxygenated organics which may be of interest. Part I of this work described the use of a selective condensation zone to remove water during analysis by gas chromatography with multidetectors. This paper will describe the evaluation and continued development of this technique to remove water after cryogenic concentration to a GC/MS instrument. The method was determined to effectively remove most of the moisture during GC/MD analysis with little effect on the recovery of polar organics such as methanol, acetone and diethyl ether. Recoveries of non-polar compounds covering a broad volatility range, such as butane, benzene, toluene, p-chlorotoluene, n-butylbenzene and n-undecane were unaffected by this Moisture Management System (MMS). Transfer of the technology to the GC/MS, which is more sensitive to moisture than the GC/MD system has proven to be more difficult and has required hardware modifications to remove sufficient amounts of water to achieve reproducible results.

### INTRODUCTION

Cryogenic concentration and thermal desorption of water into a chromatographic system during the analysis of ambient air for volatile organic compounds (VOCs) has been shown to adversely affect chromatography, sensitivity and/or detector reliability.<sup>1-5</sup> When using subambient chromatography, water concentrated from the sample can form ice plugs in the column resulting in poor peak resolution and retention time shifts, thus making compound identification difficult. The moisture can also extinguish a flame ionization detector or exceed pressures tolerated by a GC/MS system during analysis resulting in system shutdown. Nafion membranes and sorbents may be used to remove moisture from the sample prior to cryogenic concentration, but they have been shown to partially or completely remove small, polar organic compounds such as alcohols, aldehydes and ketones. These devices may also be a source of contamination or carryover from sample to sample if not properly conditioned. Another technique employed to decrease the volume of water introduced into the MS source is the use of a jet separator coupled with a megabore capillary column. However, this approach yields higher detection limits for smaller target analytes.

A novel approach to the management of water concentrated from ambient samples such that it does not adversely effect chromatography or detector systems has been developed and is described in Part I of this paper.<sup>5</sup> It is based on condensation of moisture from the saturated carrier gas stream during thermal desorption. A Moisture Management System (MMS) was installed on a Radian designed and built automated cryogenic interface used to analyze ambient air samples with GC/MD instrumentation. The MMS system was then evaluated for recoveries of compounds having a wide range of polarities and volatilities and was found to give excellent recoveries, reproducibility and chromatography when operated at a temperature of 15° C.

A similar system has been reported by Bernard, et al.<sup>7</sup> for the removal of water during purge and trap analysis. They reported that the amount of water transferred to the column correlates with the vapor pressure of water in the temperature range of their cryo-focusing module™ (CFM™). The paper reports very good peak shapes and recoveries for light gases when temperature programming the CFM from -160° C to -20° C.

In the first part of this paper, a statistically based experiment was designed to study the inter-relationship between the Moisture Management System (MMS), relative humidity, compound class, compound concentration, interface autosampler position, and canister size and the effects of each of these parameters on analyte concentration measurement precision and accuracy. The results of these experiments led to further studies designed to determine optimum operating parameters for the MMS.

Based on the results from the initial study reported last year, the technology behind the MMS was evaluated in conjunction with a Finnigan 4500 GC/MS system. The study objective was to determine if sufficient moisture could be removed during desorption to utilize a 60 meter by 0.32 mmid column interfaced directly into the detector

source. As a general rule, large amounts of water interfere with ionization of target analytes, decrease sensitivity and increase variability of the analysis.

The wide bore column interfaced directly to the source of the mass spectrometer is vital to achieving the desired sensitivity, chromatographic resolution and the ability to analyze small polar organic compounds. Two commonly used approaches to GC/MS analysis of whole air samples, using Nafion driers and using Megabore columns with jet separators, sacrifice some of the desired analytical parameters. The use of Nafion driers results in the loss of polar organic compounds. The use of a megabore column with a jet separator results in the loss of chromatographic resolution and higher detection limits.

## EXPERIMENTAL DESIGN

The MMS used on the GC/MD systems consisted of an aluminum block which encased a short length of 0.125 inch o.d. tubing between the cryogenic trap and the transfer line to the GC (Figure 1). The device was passively cooled by nitrogen gas exhaust from the cryotrap as liquid nitrogen was sprayed on the trap during sample concentration. Temperature of the device was regulated by an 80 W cartridge heater controlled by an Omega® temperature controller.

The system was configured such that the sample flows through the MMS during concentration. During thermal desorption, the chromatographic carrier gas flow backflushed the trap transferring desorbed organics and water vapor through the MMS. Thermal desorption of the cryotrap at 600°C/minute supersaturated the helium gas with water vapor which then condensed in the cool MMS region. Through the manipulation of temperature, desorption time and system configuration, the amount of water removed and the recoveries of organic compounds of interest were maximized.

A cryogenic interface similar to those used on the GC/MD instruments was equipped with the cryogenic trap and MMS system as shown in Figure 1. This interface was combined with a Finnigan 4500 GC/MS analytical system for evaluation. Operating conditions were initially set up to be the same as those which were optimal for the GC/MD systems (MMS operated at 15°C). The goal of this experiment was to establish a reliable GC/MS analytical technique capable of accurately measuring low to sub ppb levels of ambient organic compounds from undried air samples. Columns and conditions used were the same as used for GC/MD analysis, thus providing true confirmational analysis with similar detection limits and analyte lists.

## RESULTS AND DISCUSSION

Analysis of humid standards using the system and conditions described above resulted in very poor chromatography and sensitivity on the GC/MS instrument. It was obvious that a considerable amount of water was still being transferred to the column and subsequently into the source of the GC/MS. Analysis of humid samples with a Nafion drier used to dry the samples before concentration gave very good peak shapes and reproducibility, indicating that water from the samples was the problem. These results indicate the mass spectrometer, as a GC detector, is much more sensitive to moisture than the FID and PID detectors on GC/MD systems. Moisture condensation in the MMS using the same temperature and configuration as with the GC/MD systems did not remove sufficient moisture to avoid moderation of compound ionization.

Since operation of the MMS at 15°C was optimal for the GC/MD systems, but not optimal for the GC/MS conditions, the temperature of the MMS was lowered to 0°C and the experiments were repeated. At a MMS temperature of 0°C and loading 0.5 L of a 70% relative humidity sample, the chromatograms were much more reproducible and peak shapes were greatly improved. In addition, polar compounds, such as ethanol, isopropanol and diethyl ether were observed and peak shape was generally good.

Figure 2 presents an ambient air sample from Houston, Texas analyzed under these conditions. The sample was diluted by a factor of approximately three with dry nitrogen as is standard operating procedure. A load volume of 0.5 L of diluted, humid sample was concentrated and injected into the analytical system. As can be observed, the chromatography for this sample was acceptable and sensitivity was very good.

An attempt was made to analyze the same sample at a load volume of 1.5 L to obtain increased sensitivity and to determine if load volume had an effect on the GC/MS system. The results of this analysis are shown in Figure 3. Sensitivity was lost due to the increased amount of water delivered to the mass spectrometer. It was concluded that the condensation zone of the MMS was of sufficient size to condense the water from a 0.5 L load volume of this sample, but did not allow adequate surface area or contact time to condense the moisture from a

larger load volume. This loss of sensitivity also suggests that the GC/MS system may have a critical mass of moisture above which sensitivity is rapidly lost.

Since it is desirable to load larger amounts of sample to increase sensitivity, a means of increasing water removal efficiency was developed. The original MMS system contained a cooled zone approximately 1.5" long in 1/8" o.d. tubing. The size and length of the cooled zone limits the residence time and surface area available to condense water. In order to increase surface contact and residence time in the cooled zone, a new design was developed as shown in Figure 4. The MMS cooled zone consists of an 8 inch piece of 1/16" o.d. stainless steel tubing spiral wound around an 80 W cartridge heater. Active cooling, as opposed to passive cooling with the original design, was achieved with a cryogenic solenoid valve and temperature controller. The cartridge heater was used to remove the water from the MMS system after sample injection by heating to 150° C and backflushing with dry nitrogen for 10 minutes.

A second problem observed with the original MMS design which did not affect the operation of the GC/MD systems, but is a consideration with GC/MS, is the buildup of water in the transfer lines after multiple analytical runs. The passive cooling of the original MMS design contributed to this problem by allowing cool nitrogen gas to contact the sample transfer lines and provide multiple, uncontrolled sites for condensation. This problem was addressed by sealing the openings in the top of the cryotrap and venting spent nitrogen outside of the interface. Transfer lines were carefully heat traced to provide only one cool (<80° C) zone, the MMS, where water could condense.

Initial experiments conducted with the redesigned MMS system indicate that this system may be capable of removing most of the water from ambient samples and allow loading of larger sample sizes. Operational temperatures are being evaluated, but temperatures around 0° C may be needed to adequately remove the moisture in most samples. Such temperatures may affect polar compound recovery as observed in the initial study, but allow for qualitative and semi-quantitative analysis of these compounds. Additional work is planned to determine polar recoveries and reproducibility.

## CONCLUSIONS

The Moisture Management System has proven to be an effective tool for reducing the amount of water delivered to the column during analysis of VOCs using GC/MD systems. GC/MS instruments have proven to be more sensitive to the amount of moisture injected. The original MMS design worked well with smaller sample volumes, but did not allow larger samples to be analyzed, thus limiting sensitivity for undried samples. The redesigned MMS shows promise of removing additional water and providing larger sample sizes. However, complete evaluation of this new system has not been completed. As with the original MMS design, the operating parameters must be optimized to obtain maximum reproducibility and recovery of polar organics. Parameters to be optimized include MMS operating temperature, transfer line temperatures, bake-out times and temperatures, initial GC/MS oven temperature, column flowrate and load volumes. Evaluation of these parameters and their effect on the analysis of undried samples will continue.

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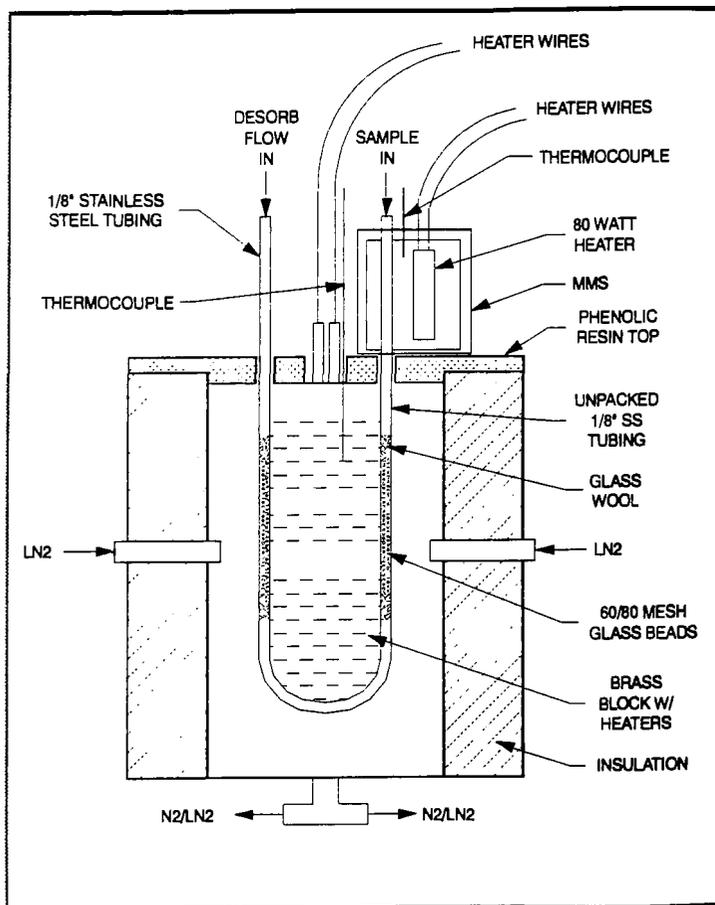


Figure 1. Original MMS and Cryotrap Design.

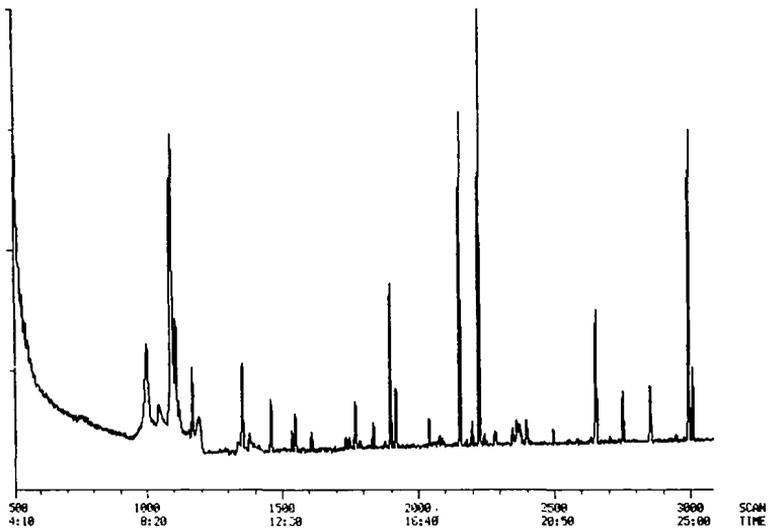


Figure 2. 0.5 L Ambient Air Sample; MMS at 0° C.

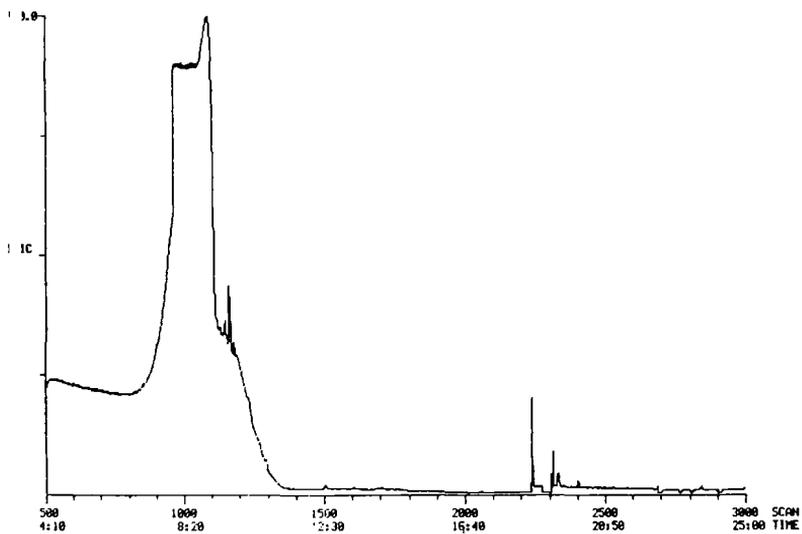
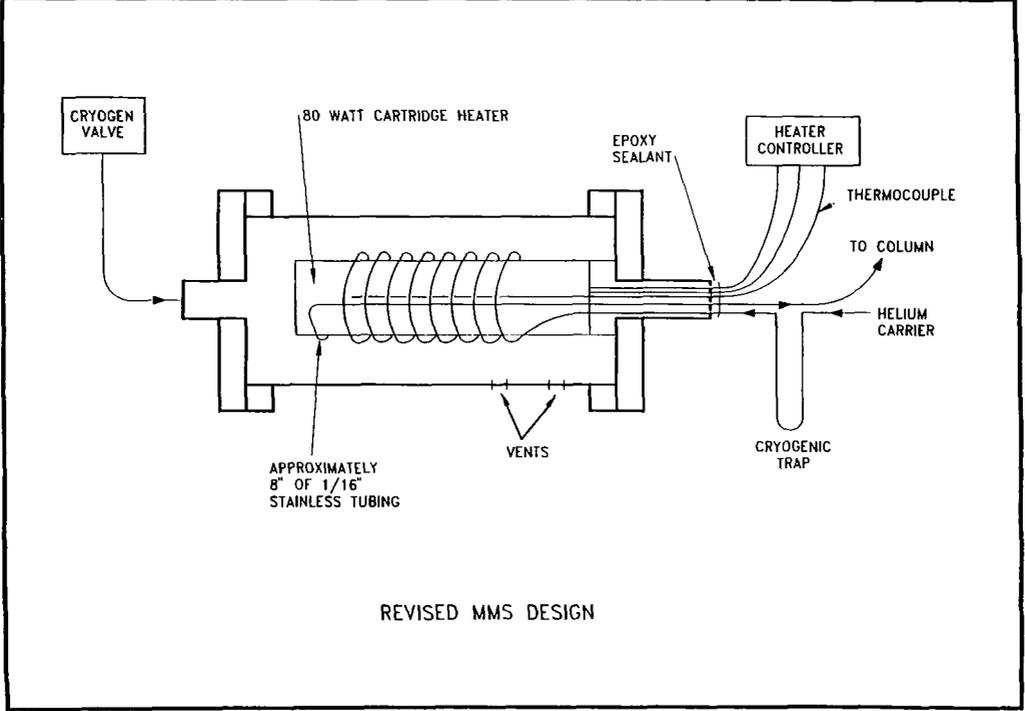


Figure 3. 1.5 L of Ambient Air Sample (same as Figure 2); MMS at 0° C.



REVISED MMS DESIGN

Figure 4. Revised MMS Design.

# DETERMINATION OF VOCs IN AMBIENT AIR AT 0.1 PPBV FOR THE CLEAN AIR STATUS AND TRENDS NETWORK (CASTNet)

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## ABSTRACT

The 1990 Clean Air Act Amendments (CAAA) will require laboratories to analyze ambient air samples for a wide range of volatile hazardous air pollutants (HAPS) at levels below 1 ppbV. One of the air pollution monitoring requirements of the 1990 CAAA is for state and local air pollution control agencies to track air toxics emission reductions, develop air toxics emission profiles, and identify unknown sources of toxic air pollutants. Under the Clean Air Status and Trends Network (CASTNet), Environmental Science & Engineering, Inc. (ESE) has the responsibility to reactivate and operate the Urban Air Toxics Monitoring Program (UATMP). This network has been supported by the Environmental Protection Agency's (EPA's) Office of Air Quality Planning and Standards (OAQPS) since 1988. During 1993-94, ESE will monitor air toxics at several urban sites in the Eastern United States and analyze samples collected from that network. State and local agencies will be responsible for collecting 24-hour integrated air samples every 12 days. These samples will be analyzed by ESE for volatile organic compounds (VOCs), carbonyls, and metals. This paper presents a description of the analytical approach that will be employed for the determination of VOCs collected in passivated stainless-steel canisters. The results of system performance and method detection limit (MDL) studies are also presented.

## INTRODUCTION

EPA Compendium Method TO-14, "Determination of VOCs in Ambient Air Using Summa® Passivated Canister Sampling and Gas Chromatographic Analysis",<sup>1</sup> has generally been the reference method of choice for the sampling and analysis of ambient air samples for a wide range of VOCs. Analysis by gas chromatography/multidetector (GC/MD) or gas chromatography/mass spectrometry with selected ion monitoring (GC/MS-SIM) traditionally has been necessary to determine concentration levels in ambient air as low as 0.1 ppbV. However, both of these approaches limit qualitative and quantitative information to the target compounds only, and target compound identification is not positive and often questionable when analysis is performed by GC/MD. Furthermore, the semi-permeable membrane (Nafion) dryer, traditionally used to eliminate excessive moisture from samples, limits reliable quantitative and qualitative determinations to non-polar VOCs due to the coincidental elimination, or partial elimination, of polar analytes from the sample stream.

This paper presents results of a preliminary evaluation of an Entech Model 2000 automatic cryogenic preconcentration system equipped with a 16-position autosampler manifold and interfaced to a Hewlett-Packard (HP) 5890 GC/Finnigan Incos 50 MS operated in the full-scan mode (GC/MS-SCAN). This system will be employed by ESE to determine VOCs in ambient air as part of the CASTNet air toxics monitoring program. The system utilizes a moisture control approach that allows 0.1 ppbV concentrations levels to be achieved for target VOCs. In addition, it will allow qualitative and semi-quantitative data to be collected for non-target VOCs, non-polar and polar alike.

## EXPERIMENTAL

### Canister Preparation

To determine ambient VOC concentrations with acceptable precision and accuracy at concentration levels as low as 0.1 ppbV, it is imperative that the laboratory establish the cleanliness and integrity of each sampling canister. ESE utilizes an Entech Model 3000 Canister Cleaning System for cleaning and leak checking canisters.

Canister leak checking is performed prior to canister cleaning. The canisters are connected to the system manifold via 1/4-inch stainless-steel tubing and the canister valves are left closed. The high vacuum pump is engaged and the vacuum pressure is monitored using the in-line pirani gauge (0-2000 mtorr sensor). If a significant leak exists, it will manifest itself by not allowing the system to

quickly evacuate to approximately 0.3 torr, and/or the system pressure will quickly rise once the high vacuum pump is disengaged. Quick disconnects are situated between each canister and the manifold to allow easy isolation of individual canisters which may have leaking valves. After the repetitive fill/evacuate cycling is completed, the high vacuum pump is used for final canister evacuation. Leaks will not allow the canisters to achieve a vacuum reading of approximately 0.5 torr.

As many as eight 6-liter canisters are cleaned simultaneously over a 4-hour period through automatic, unattended cycling between canister filling and evacuation modes. Each of the canisters is heated to 100°C for the duration of the cleaning process. A rough-vacuum oilless diaphragm pump cycles between eight 8-minute fillings and eight 8-minute evacuations. Nitrogen vent gas from a liquid nitrogen dewar is used for the fill gas and a humidification chamber containing ASTM Type-II HPLC grade water is used to add moisture to the fill gas in order to assist in the displacement of VOCs from the interior surface of the canisters. In the fill mode the canisters are pressurized to about 25 psig. After completion of eight cycles with the low-vacuum pump, the canisters are evacuated with a high-vacuum oil-based pump for about 75 minutes to an absolute pressure of 0.5 torr, which is measured by an in-line pirani gauge. A cryogenic trap containing liquid nitrogen is placed between the pump and the system controller to keep oil vapor out of the system.

At the completion of the cleaning cycle, the canisters are pressurized to 30 psig with humidified nitrogen and analyzed by GC/MS. No target analyte should be detectable at or above its reported limit of quantitation. After analysis, each canister is re-evacuated to 0.5 torr.

### **Standards Preparation**

Working calibration standards are prepared in canisters at a minimum of five concentration levels in the range of 0.1 - 20 ppbV. These working standards are prepared from stock calibration mixtures containing approximately 100 ppbV of each of the target analytes in dry nitrogen in high pressure (2000 psi) cylinders. These calibration mixtures are purchased from Scott Specialty Gases and are certified to  $\pm 5\%$  for each of the VOCs.

The working calibration standards are generated by dynamic flow dilutions of the purchased mixtures with cleaned, dry zero grade nitrogen humidified with ASTM Type II HPLC-grade water. ESE utilizes an Entech Model 4560 Dynamic Dilution System for this process. This system utilizes up to six mass flow controllers for simultaneous blending from multiple cylinders. Canisters are generally filled to pressures of 15 to 25 psig. Newly prepared calibration standards are allowed to equilibrate at least 24 hours before analysis.

The 40 compounds listed in method TO-14 (ethyl toluene was not included) were evaluated for this paper.

### **Instrumental Analysis**

Canister samples are analyzed with an Entech Model 2000 automated VOC cryogenic preconcentrator equipped with an Entech 2016 16-position autosampler manifold and interfaced to a HP 5890 GC/ Finnigan INCOS 50 MS operated in the full scan mode (35 to 270 amu). The preconcentrator system is under software control (IBM compatible) and a QA/QC report is a standard feature for documentation of actual run conditions.

Canisters are attached to the manifold with 1/8 inch stainless-steel tubing. A leak check of the system is then performed. Sample flow is set under mass flow control to 150 mL/min. to give an integrated total volume of 1000 mL. Both subambient and pressurized canisters can be analyzed because the system employs a mechanical pump to draw samples across the preconcentrator. The internal standards, bromochloromethane, 1,4-difluorobenzene, and *d*<sub>5</sub>-chlorobenzene, are also added to each analysis at 150 mL/min. to a total volume of 100 mL. All rotary valves and transfer lines exposed to the sample matrix are heated at 70-100°C.

The Entech preconcentrator employed by ESE for analyzing VOCs in ambient air is configured with a 3-stage trapping approach which allows a large sample volume to be concentrated and the moisture removed without loss of polar VOCs. The first stage is a high-volume cryogenic trap (1/8 inch nickel tube containing glass beads) cooled during sampling to -150°C with liquid nitrogen. After cryotrapping 1000 mL of sample, the first stage trap is heated rapidly to about room temperature and gently purged (about 10 mL/min.) with 30 - 50 mL of nitrogen to transfer the trapped VOCs to a second stage trap (1/8 inch nickel tube) containing hydrophobic Tenax TA held at 0°C. The second stage trap is then heated to 170°C and backflushed with helium to a third stage megabore focusing trap cooled with liquid nitrogen to -150°C. After heating and backflushing of the second stage trap is complete, the third stage trap is then very rapidly heated to above 100°C to allow a rapid injection of the VOCs onto the GC analytical column.

The target analytes are separated on a DB-1 fused silica capillary column, 75 m x 0.32 mm I.D., with a 1 micron film thickness. The chromatographic run is started at 35°C and held for 5 min. A subambient starting temperature is not required because of the rapid transfer of VOCs from the preconcentrator's third stage megabore focusing trap of the Entech preconcentrator to the head of the GC column. Sharp peaks with 2-5 sec. widths are maintained, even for early eluting compounds. The column is then temperature programmed at 6°C/min. to 180°C and then at 7.5°C/min. to 225°C.

The total run time for preconcentration of the sample and chromatographic separation is approximately 60 min.

The MS scan rate is approximately 3 scans/sec. The Incos 50 turbomolecular source pump draws about 170 L/ min. This pumping rate effectively prevents source pressure increases from any residual sample moisture.

### System Performance and Method Detection Limit Studies

The reproducibility and linearity of the analytical system were evaluated over a two-week period. Eight calibration standards and a blank were prepared as described above in separate 6-liter canisters. The blank canister was prepared with humidified zero grade nitrogen. The calibration standards contained the 40 compounds listed in Method TO-14 and were prepared at concentration levels of 0.1, 0.25, 0.5, 1, 2, 5, 10, and 15 ppbV. Another canister containing the three internal standards was also prepared. All canisters were attached to the autosampler manifold and analyzed, after instrument tuning, as described above. Internal standards were added to each analysis at 5 ppbV. The canisters were analyzed three times, with a week between analytical runs. Initial canister pressures ranged from 10 to 15 psig for the first day's run, from 1 to 2 psig for the second day's run, and from -1 to -2 psig for the last day's run in order to evaluate reproducibility under different canister pressures.

After analysis of the calibration standards on the second analysis day, an MDL study was performed. Lower limits of detection for the target compounds were estimated for each instrument by determining the method detection limits (MDLs) as specified by the U.S. Environmental Protection Agency (U.S. EPA).<sup>2</sup> Seven canister samples were prepared at about 1 ppbV for each of the target compounds used the standards preparation system described above. The seven replicate samples were then analyzed and quantitated against the average relative response factors (RRF) of the five calibration standards ranging from 0.1 to 2 ppbV. The internal standard method of quantitation was employed. The MDL for each target compound is calculated by multiplying the standard deviation of the seven replicate concentration measurements by the appropriate one-sided t-value corresponding to n - 1 (6) degrees of freedom. The corresponding t-value for seven measurements is 3.134.

### RESULTS

The reproducibility, or precision, of the analytical system was evaluated by comparing the responses of the target compounds and their corresponding internal standards over the three analysis days at different calibration standard concentrations. In addition compound retention time variability was evaluated. Table 1 summarizes response and retention data for vinyl chloride, benzene, and hexachlorobutadiene (HCBD) at 0.1, 1 and 10 ppbV. These compounds represent low boiling (vinyl chloride = -13.4°C), middle boiling (benzene = 80.1°C, and high boiling (HCBD = 215°C) VOCs, respectively. For each of the three compounds listed in Table 1, the relative standard deviations (RSDs) of the absolute responses for the three analysis days over the three concentration levels averaged less than 6 percent. The relative response factors averaged less than 5 percent. The RSDs of the absolute responses of each of the internal standards for the three analysis days and within each analysis day over the three concentration levels averaged less than 5 percent. Retention times had ranges no greater than .03 minutes for the three compounds. Response and retention time results for the other target VOCs were similar.

Table 2 summarizes calibration data for vinyl chloride, benzene, and HCBD on the second analysis day. The compound responses were very linear over the 0.1 to 2.0 ppbV range, as measured by either a linear regression curve or the RSD of the RRFs. Table 2 also shows the corresponding MDL calculations. Only six of the seven 1 ppbV replicate samples were used because one of the replicates was improperly prepared. The higher t-value of 3.365 was therefore used. Sample concentrations were calculated using the RRFs of the samples and the average RRF of the standard curve.

The calculated MDLs averaged 0.13 ppbV for all the TO-14 compounds. Nearly 40% of the MDLs were less than 10% of the 1 ppbV nominal concentration analyzed. This indicates that the replicate analysis for those compounds should have been targeted at a lower concentration (probably 0.5 ppbV). The 0.1 ppbV responses for all the TO-14 compounds were well above background noise, in

the range of 10 - 50,000 area counts. Compound responses were linear over the 0.1 - 1 ppbV range, and generally demonstrated a quadratic fit across the full calibration range (0.1 - 15 ppbV), which would be expected of the typical quadrupole MS.

#### **Polar VOCs**

Although this paper does not discuss experimental results for polar VOC determinations using the analytical system described above, preliminary analysis of eight polar VOCs of interest have been promising. The compounds that are currently being investigated include acetone, acetonitrile, acrolein, acrylonitrile, methyl ethyl ketone, methyl isobutyl ketone, methyl methacrylate, and vinyl acetate. Addition of particular polar VOCs to the canister target analyte list in the CASTNet program will be dependent upon results obtained from an evaluation of the unknowns data obtained from GC/MS-SCAN analysis and experimental determinations of their stability in canisters.

#### **CONCLUSIONS**

Routine measurement of ambient VOCs at 0.1 ppbV by GC/MS-SCAN can be achieved with acceptable precision and accuracy using commercially available instrumentation. This has been demonstrated with a analytical system comprised of an Entech preconcentrator, an HP GC, and a Finnigan MS. The system will be employed for VOC determinations in canister samples collected for the CASTNet air toxics monitoring program.

#### **ACKNOWLEDGEMENTS**

The authors thank Norm Staubly for his laboratory assistance.

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**Table 1: Area Response and Retention Time Reproducibility of Selected VOCS**

	Pressurized			Atmospheric			Sub-Atmospheric		
	2/17/93			2/23/93			3/04/93		
	VC	Bzn	HCBD	VC	Bzn	HCBD	VC	Bzn	HCBD
<b>10 ppbV</b>									
Resp. (x10 <sup>3</sup> )	2058	2379	883	2067	2256	910	1996	2195	843
IS Resp. (x10 <sup>3</sup> )	764	2078	1665	702	1947	1610	732	1978	1582
FFF	1.35	0.57	0.27	1.47	0.58	0.28	1.36	0.56	0.27
Ret. Time	4.03	10.16	28.11	4.02	10.15	28.11	4.03	10.16	28.12
<b>1 ppbV</b>									
Resp. (x10 <sup>3</sup> )	278	302	124	271	279	111	290	300	106
IS Resp. (x10 <sup>3</sup> )	808	2143	1652	762	2000	1577	788	2094	1614
FFF	1.72	0.70	0.38	1.77	0.70	0.35	1.84	0.72	0.33
Ret. Time	4.03	10.15	28.11	4.04	10.16	28.11	4.03	10.16	28.11
<b>0.1 ppbV</b>									
Resp. (x10 <sup>3</sup> )	29.7	27.1	13.5	27.9	26.1	13.8	31.3	29.8	14.8
IS Resp. (x10 <sup>3</sup> )	739	1968	1479	724	1894	1440	748	1985	1551
FFF	2.01	0.69	0.46	1.93	0.63	0.48	2.09	0.75	0.48
Ret. Time	4.02	10.15	28.10	4.02	10.14	28.09	4.02	10.15	28.11

**Table 2: Calibration and MDL Results for Selected VOCs**

<b>Calibration:</b>						
<b>Standard (ppbV)</b>	<b>VINYL CHLORIDE</b>		<b>BENZENE</b>		<b>HCB D</b>	
	<b>Response</b>	<b>RRF</b>	<b>Response</b>	<b>RRF</b>	<b>Response</b>	<b>RRF</b>
2	515511	1.67	575498	0.700	219910	0.340
1	270598	1.77	279430	0.699	111351	0.353
0.5	141763	1.93	132341	0.672	51646	0.355
0.25	74681	2.03	68616	0.733	27152	0.371
0.1	27932	1.89	26112	0.652	13810	0.461
0	0		3248		254	
L.R. Corr. Coeff.	0.9995		0.9993		0.9997	
y-Intercept	6895		-5397		264	
Average RRF	1.86		0.691		0.376	
%RSD of RRFs =	7.5		4.5		13	
<b>Method Detection Limit Determinations:</b>						
<b>1 ppbV</b>	<b>VINYL CHLORIDE</b>		<b>BENZENE</b>		<b>HCB D</b>	
	<b>RRF</b>	<b>Conc.</b>	<b>RRF</b>	<b>Conc.</b>	<b>RRF</b>	<b>Conc.</b>
1	1.93	1.04	0.638	0.923	0.355	0.944
2	1.82	.978	0.628	0.909	0.337	0.896
3	1.92	1.03	0.626	0.906	0.335	0.891
4	1.92	1.03	0.594	0.860	0.396	1.05
5	1.92	1.03	0.592	0.857	0.404	1.07
6	1.92	1.03	0.599	0.867	0.382	1.02
Average Conc:	1.02		0.887		0.978	
Standard Deviation:	0.022		0.029		0.079	
t-value:	3.365		3.365		3.365	
<b>Calculated MDL:</b> <b>(ppbV)</b>	<b>0.07</b>		<b>0.10</b>		<b>0.27</b>	

# DEVELOPMENT OF METHODS FOR SAMPLING AND ANALYSIS OF VENT STREAM EMISSIONS FROM GLYCOL DEHYDRATION UNITS IN THE NATURAL GAS INDUSTRY

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## ABSTRACT

Emissions of benzene, toluene, ethylbenzene and xylenes (BTEX) and other volatile organic compounds (VOCs) from the regenerator still vent of glycol dehydration units have become an important environmental concern for the natural gas industry. The objective of this program was to develop and validate sampling and analytical methods for the measurement of BTEX and VOCs from these sources. Development of new methods for still vent streams was necessary due to concerns about the accuracy of existing methods with such a sample matrix. Glycol vent streams generally have low flow rates and are comprised of approximately 90% steam with a balance of vapor phase organic compounds. Such a stream does not lend itself to sampling and analysis by standard methodologies, such as VOST techniques.

A total of five direct measurement sampling techniques and five screening methods for still vent emissions were evaluated in a preliminary field test conducted in early 1992. The most promising methods were then further evaluated in extensive laboratory testing to arrive at a limited number of sampling methods for further field evaluation. Sampling methods evaluated during the field evaluation included Total Capture Condensation (TCC) of the vent stream, slip-stream condensation of a portion of the vent stream, natural gas collection in canisters, high pressure rich glycol sampling in stainless steel bombs, atmospheric pressure rich and lean glycol sampling in VOA vials and a field glycol/gas separation unit.

## INTRODUCTION

Glycol dehydration units (typically triethylene glycol) are used to remove water from produced gas streams to prevent hydrate formation and corrosion in the pipeline. The natural gas contacts the glycol countercurrently in an absorber column to remove the water. Glycol exits the bottom of the absorber and on most larger units goes into a flash tank where pressure is reduced and most of the volatile organics, primarily methane, absorbed in the glycol are removed. The glycol then enters a still and reboiler where water and any residual organics are distilled from the glycol. Lean glycol is then pumped back into the absorption column.

During the absorption step at high pressure, methane and other organic compounds are absorbed into the glycol from the natural gas. Aromatic compounds, primarily BTEX have a high affinity for the glycol. Small amounts are removed in the flash tank, but most along with higher molecular weight aliphatic hydrocarbons, are removed during the distillation step. These compounds are then potential emissions from the still vent stack which may be regulated under the 1990 Clean Air Act Amendments.

The purpose of this program was to develop sampling and analytical techniques applicable to the accurate measurement of the emissions from the still vent stacks under the sponsorship of the Gas Research Institute (GRI). Emission measurements for glycol dehydration units have been made using a variety of sampling points, sampling protocols and analytical techniques since standard methods are not available. Most methods used prior to the initiation of this project have focused on the indirect measurement of emissions by a mass balance on the rich and lean glycol streams. Therefore further evaluation of these methods, plus a direct measurement method of the still vent stream was needed to accurately determine emissions.

Direct measurement of the organic emissions from the still vent stream is very difficult.<sup>1,2</sup> The stream temperature is in the range of 200-220° F and contains over 90 percent water with a balance that is primarily organic compounds (percent levels). Problems encountered when trying to sample this stream include:

- Collecting or directly measuring the organics in the presence of extremely high levels of water;
- Collecting a representative sample in a low, variable flow stream that most likely contains condensed material; and
- Accurately measuring a flowrate in a steam/organic stream.

Since analytical methods are generally well established for analysis of hydrocarbon emissions, generally using capillary gas chromatography with flame ionization detectors, this paper will primarily focus on the development of sampling and flowrate measurements for the glycol vents.

### Experimental and Discussion

Input to the program is provided by an Industry Working Group which includes representatives from several industry organizations. Initial methods evaluated included several suggested by the Industry Working Group plus a number of standard EPA methods and methods from other sources. These methods were evaluated in a preliminary field experiment at a eight million standard feet per day glycol unit in South Texas. These methods included direct measurement techniques for the vent stack and several indirect measurement (or screening) techniques and collection and analysis of natural gas in canisters for use in modeling the emissions of hydrocarbons.<sup>3</sup> Those methods evaluated in this effort are listed in Table 1. The methods which were deemed worthy of further study and those eliminated are indicated. Methods based on absorption of the organics onto sorbent materials, such as with the VOST technique or NIOSH charcoal tubes were quickly eliminated. Methods based on color changes, such as Dräger or Sensidyne tubes were also eliminated. As a general rule, organic levels in the still vent stack were much too high to use absorption as a collection technique. Swelling and heating of the material in the tubes caused the tubes to either crack or the flow to be restricted.

Results from two of the stack methods, the Total Capture Condensation (TCC) and the Air Dilution, agreed reasonably well and were considered to be an accurate measurement of the still vent emissions. However, it was determined that in order to obtain an accurate measurement of the emissions using the Air Dilution technique, an accurate measurement of the stream flow must be made. This measurement proved to be very difficult to make due to the stream composition. Therefore, an objective of the laboratory development phase was the identification of an accurate flow measurement technique. A variation of the TCC technique was also to be evaluated in the laboratory study which would require accurate measurements of the vent flow. This method, slipstream total capture condensation, was developed as a means of collecting a portion of the total vent flow on units treating more than approximately 10 MMSCFD and for which condensation of the total vent flow was impractical.

The collection of a small portion of the gas from the still vent in an evacuated canister gave results approximately seven times higher than TCC. The high results were most likely due to delivery of liquids or aerosols into the canister. Though this method did not work well in the initial field trials, it was decided to continue working on it during the laboratory study because it required minimal setup and equipment as compared to the other direct measurement techniques.

High pressure rich glycol samples are normally collected after the flash tank and before the regenerator to measure emission of BTEX and hydrocarbons actually removed in the glycol regeneration. The mass balance between the rich glycol and the lean glycol, after regeneration, is used to calculate emissions. In the initial study the rich glycol was taken before the flash tank. This did not appear to greatly affect BTEX emission calculations as little is removed in the flash tank. However, it did appear to bias the total hydrocarbon measurements high as compounds, such as methane and ethane, normally removed in the flash tank were included in the measurement. Development of the rich glycol collection in sample cylinders centered around the separation and measurement of volumes of the liquid and gas phases once the pressure was released from the vessel. Atmospheric glycol laboratory development centered around the minimizing the loss of volatile gases during collection.

### Laboratory Techniques

In the portion of the laboratory studies focusing on the stack sampling techniques, a bench-scale unit (Figure 1) was constructed to simulate the still vent stream. It consisted of a steam generator that produced 6.8 lb/h of steam and an organic injection apparatus. Organic liquid was pumped into a heated injection block to vaporize the organics. The vaporized organics were swept from the injection zone into the steam by methane. The entire system was heat traced to minimize condensation before the collection apparatus. Since the flowrate of the steam

and the organics was known, the vapor phase concentration could be calculated and used to determine compound recoveries from each collection technique.

**Total Capture Condensation.** The total capture condensation apparatus used in the laboratory study consisted of a 5 gallon container in which a 5 foot long by 1" inside diameter coil of copper tubing was placed. The copper tubing acted as a condenser for the steam and organics in the simulated still vent stream. A glass collection vessel was used to collect the condensed liquid. The gas exiting the system could also be collected in Tedlar bags for analysis. In most instances, the gas phase did not contribute significantly to the calculations as it primarily consisted of the methane used as the sweep gas and small amounts of pentane and hexane which were not completely condensed.

A total of six back to back duplicate collections were made using the TCC system. The results from the collection of selected organic compounds is shown in Table 2. The gas flowrates for the steam and organic phase along with individual compounds tested are included. These ratios of organics to water and the flowrates are indicative of those measured in the field trial study. Based on the results of the laboratory study, a field collection apparatus (Figure 2.) was constructed from a 55-gallon drum and 50' and 1" of copper tubing.

**Air Dilution System.** The air dilution system was designed to dilute the steam/organic stream by a factor of approximately 10 and then collect the resulting air, moisture and organic stream in a canister or Tedlar bag for gas phase analysis. Identical flowrates and concentrations were to be used as tested for the TCC apparatus. However, during calculations of gas phase concentrations after dilution, it was determined that the concentrations would be very close to the lower explosion limit for many of the compounds. Despite the fact that explosion-proof equipment was used in the initial field trial, it was decided that this method posed too much danger to operators and equipment to be used as an industry recommended method. Therefore, the air dilution method was dropped from consideration.

**Canister Sampling.** Canister samples were collected from the simulated vent stream by attaching a canister with a Veriflow® flow regulator to a heated port in the vent line. In order to avoid the condensation problems observed in the field trial: the sample lines, filter, regulator and canister valve were all heated with heat tape. In addition, samples were taken from three different configurations; 1) with the sample probe inserted at a 90 degree angle and parallel (horizontal) to the vent; 2) with the sample probe 90 degrees from the vent inserted from the top (vertical) to the vent; and 3) as in #2 except the probe in the stream was bent with the opening facing away from the direction of flow to minimize aerosol entrainment. The canisters were diluted before analysis by GC/FID. As before, concentrations were highly variable indicating condensation in the sample lines and canister. This method was also eliminated as a possible collection technique. Acceptable results also could not be obtained from an on-line GC which was set up for comparison to the vapor phase analysis of the canisters. It also was plagued with problems caused by the condensation of water and organics in the sample lines or aerosols carried into the injection loop.

**Slipstream Total Capture Condensation.** A variation of the TCC technique was evaluated for use of large units, greater than 10 to 20 MMSCFD. On very large units, condensation of the entire stream is not feasible and a slipstream from the vent must be used to determine the emission levels. However, in order to determine emissions from the vents, the stream flowrate must be accurately measured. In the laboratory study, the flowrate is known since the addition rate of steam and organics is controlled and constant. In a field situation, flowrate measurement is much more difficult as will be discussed later.

Care was taken to heat the slipstream lines and insulate the still vent to avoid condensation or collection of aerosols. A total of eight replicate collections were performed, each of which was collected at 0.5 liters/minute and for 30 minutes. With the calculated flowrates for the total stream flow, recoveries for BTEX, hexane, pentane and octane average 114% and the recovery of water averaged 96%. The slipstream technology was considered to be worthy of additional testing in the field evaluation portion of the program.

**High Pressure Glycol Sampling and Analysis.** Glycol samples collected at elevated pressures in high pressure sample cylinders can release considerable amounts of gas and produce copious amounts of foam upon pressure release. In order to develop methods for handling the foam, collect gas released from the cylinders, determine losses of target compounds during atmospheric pressure collection and measure gas volume, synthetic samples of TEG with BTEX, methane or propane, pentane, and hexane were generated. Methane or propane was added to the cylinder to pressures around 50 psig to provide a volatile gas. The pressure in the cylinder was brought to 900 psig using an HPLC pump delivering TEG to which the other compounds and water had been added. Upon release of the pressure, the volatile organic would degas from the liquid simulating a field sample.

Techniques were developed for collection and measurement of the volatile fraction which degasses from the glycol phase. A positive displacement apparatus consisting of a sealed chamber containing a Tedlar bag for sample collection and a dry gas meter to measure the volume of gas displaced by the sample gas flowing into the bag was built. With some minor modifications this system worked well in collecting and measuring gas volumes. In addition, two techniques designed to help eliminate foaming were evaluated. These included heating the cylinder to reduce viscosity of the liquid and adding methylene chloride to the cylinder before sample collection to reduce sample viscosity and act as a keeper for less volatile organics in the glycol (pentane and larger). Heating did not seem to help, but results from the methylene chloride addition were favorable. Recoveries of the non-gaseous components in the glycol ranged from 103 to 126%. The high pressure rich glycol sampling technique, with and without addition of methylene chloride, was also slated for further study in the field evaluation testing portion of the program.

Total Flow Measurement. As mentioned earlier, total flow measurement in the still vent stream is very important in determining emission rates by any method that does not collect the entire stream. Due to the fact that the still vent stream is hot and wet, consists of a 2" pipe and has flowrates that can fluctuate wildly due to heating a cooling cycles of the reboiler, traditional flow measurement devices such as dry gas meters and pitot tubes are not applicable. In the laboratory study, a hot wire anemometer and a mass flowmeter were evaluated for measurement of flowrates. The mass flowmeter did not work at all and the hot wire anemometer exhibited a relatively short cycle fluctuation of less than a minute. However, the mean measurement for the hot wire anemometer during these cycles was very close to the calculated flowrates. A decision was made to further test the hot wire anemometer in the field evaluation studies. Orifice plates, which were not evaluated in the laboratory, were also to be evaluated in the field.

#### CONCLUSIONS AND PLANS FOR FUTURE WORK

Results from the laboratory studies led to the elimination of collection of small samples from the still vent in canisters and the air dilution of the vent stream. Methods slated for further evaluation at working glycol dehydrators include Total Capture Condensation, Slip Stream Condensation, Rich Glycol Sample Cylinders and Atmospheric Rich/Lean Glycol Collection. In addition, two flow measurement techniques, the Hot Wire Anemometer and Orifice Plates, will be evaluated. A field gas-glycol separation apparatus suggested by a member of the Industry Working Group is to be evaluated. It consists of two burettes connected in series with a water displacement system. This apparatus will be evaluated with rich glycol samples as an alternative to the collection of high pressure rich glycol samples in cylinders. The Total Capture Condensation Method will be used as the baseline method for comparison of the results from all of the other methods.

The results of these field evaluation experiments and the laboratory studies will be statistically evaluated to statistically determine the precision and accuracy of each method developed in this program. The method(s) giving the best precision and accuracy combined with ease of use and cost will be selected as the method of choice for determining still vent emissions from glycol units. The selected method(s) will be further tested in a series of field validation experiments to be conducted April through August of 1993. These experiments will be performed at glycol units operating under different conditions (e.g., a range of treatment rates, different types of glycol, with and without flash tanks and on sweet and sour gas units). Further modification of the methods developed may be necessary based on these validation studies.

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Table 1. Preliminary methods considered for glycol dehydrator vent emission monitoring.

Technique	Continue Development?	Comments
<b>Direct Measurement Techniques:</b>		
1. Air Dilution	Yes	Results considered good.
2. Total Capture Condensation	Yes	Results considered good.
3. Canister Samples	Yes	Results high; focus on collection techniques.
4. Modified VOST	No	Serious problems caused by high water/organic stream.
<b>Indirect Measurement Techniques:</b>		
1. High Pressure Rich/Atmospheric Pressure Lean Glycol	Yes	Focus on development of handling techniques.
2. Atmospheric Pressure Rich/Lean Glycol	Yes	Focus on handling techniques.
3. Natural Gas Canisters	Yes	Used with modeling.
4. Screening Indicator Methods NIOSH, Sensidyne and Drager Tubes	No	Problems similar to those with VOST.

Table 2. Spiked compounds and recoveries from the total capture condensation technique.

Parameter	Gas Flow (Liters/Min.) <sup>a</sup>	Percentage of Total Gas Phase Organic <sup>c</sup>	Calculated Recoveries <sup>b</sup>	Standard Deviations <sup>e</sup>
Steam	87.40 <sup>f</sup>		98.1	5.41
Organics (Total)	9.70		96.8	5.43
Benzene	1.07	11	96.8	7.29
Toluene	3.30	34	99.4	9.84
Xylenes	1.36	14	103	12.4
Methane <sup>d</sup>	0.30	3	ND	ND
n-Hexane	1.26	13	92.8	9.15
Pentane	1.16	12	86.3	13.3
Octane	1.26	13	99.3	6.38

<sup>a</sup>Based on 212° F from the steam generator.

<sup>b</sup>Based on total capture condensation from field samples. The paraffin hydrocarbons reflect the mass from unidentified VOCs.

<sup>c</sup>Based on 6.8 lbs/hr of water input.

<sup>d</sup>Methane is 94% commercial grade methane. Impurities include ethane, propane, isobutane, and butane.

<sup>e</sup>Based on 12 observations.

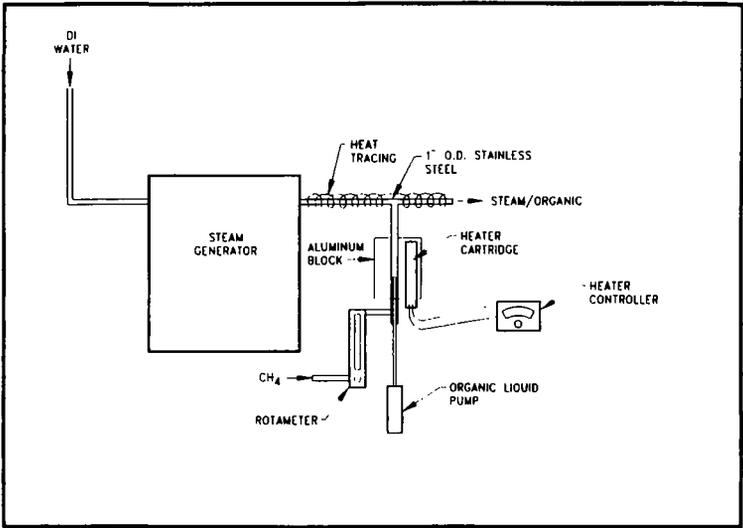


Figure 1. A bench-scale unit simulating the still vent stream.

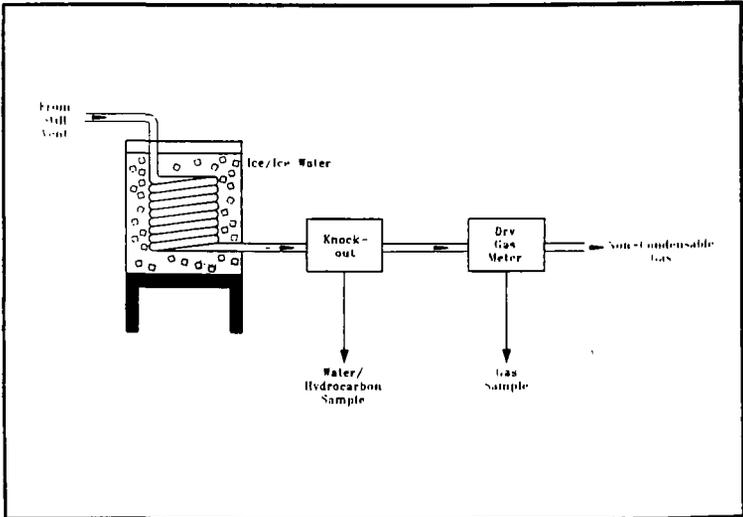


Figure 2. Total Capture Condensation Sampling Train

*Session 8*  
*S S Canisters,*  
*Use and Techniques*

## IMPROVED SENSITIVITY AND QUALITY ASSURANCE IN SUMMA CANISTER ANALYSIS USING EPA METHOD TO14

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### ABSTRACT

GC/MS is the analytical methodology mandated by the USEPA Contract Laboratory Program Statement of Work. GC/MS provides accurate quantitation and qualitative information using full scan mode. Method detection limits reported in the CLP SOW are in the range of 0.2 to 1.7 ppbv<sup>1</sup>. Using an automated air preconcentrator coupled to a high sensitive quadrupole mass spectrometer, method detection limits are determined ten times lower, exceeding TO14 requirements.

Quality Assurance from both the air preconcentrator and data system is described. Immediate feedback from the QA reports automatically documents the quality of the analytical data.

### INTRODUCTION

The analysis of toxic organic compounds in ambient air by GC/MS techniques requires sample preconcentration to obtain detection limits in the sub-ppb range. Although such methodology has been utilized for years, the achievement of detection limits specified in Title III of the 1990 Clean Air Act Amendment (2-20 ppt) have not yet been reported. This has been due to a combination of problems concerning moisture and CO<sub>2</sub> management, difficulties in sampling large volumes quickly, and limitations in absolute GC/MS sensitivities.

This paper describes a preconcentrator GC/MS configuration that approaches the low ppt requirements of Title III of the CAAA. Detection limits for target compounds significantly exceed TO14 requirements while collecting full scan data using a new, high sensitivity quadrupole mass spectrometer. Concentration parameters are recorded to provide the operator an operational log during unattended operation for improved QA/QC. Data system provides automated quality assurance reports. The system can be configured for research or production oriented laboratories utilizing 1,16, or 32 position automation.

### EXPERIMENTAL METHOD

The system used was an air preconcentrator/autosampler (Entech 2000/2010) coupled to a HP 5890GC/ HP 5972 MSD. Analyses were performed using a Restek 60 m x 0.32 mm ID Rtx Volatiles capillary column(1.5 micron film thickness). The outlet of the capillary column was directly inserted into the MSD source. A personal computer controlled the Entech System giving system printouts on air concentration parameters. Immediate feedback monitors system performance such as initial can pressure, trap temperatures, actual volume sampled, desorption temperatures, and bakeout temperatures. The MSD was controlled by an Apollo workstation using Target2 software to give quantitation and quality control reports. QC reports include tune criteria, calibration specifications, and internal standard retention time/area performance. Optimum parameters such as water management, cryofocusing, and electronic pressure control improved chromatographic resolution. Retention time stability was superior during this study. The HP 5972 allows higher column flows up to 2 cc/min and improved pump oil provides low background. A newly designed electron multiplier provides excellent signal/noise ratios.

#### Instrument Settings

<u>Entech Concentrator</u>	Glass trap	-150° C
	Tenax trap	10° C
	Cryofocusing trap	-150° C

<u>GC Conditions:</u>	35° C for 5 mins then 6 degree ramp to 210° and hold for 1 min.
<u>EPC Program</u>	2 cc flow (Approximately 15 psi)initial time 0.5 mins then drop to 1.5 cc(approximately 8 psi) flow and hold at constant flow

<u>MSD Conditions</u>	Tune: Std BFB Tune EM = 1650 Volts
	Scan parameters 35-300 amu A/D 2*3 (approximately 1 scan/sec)
	Solvent Delay 4.5 mins
	Threshold set at 100 counts

## Standard Preparation

The standards were prepared in house and then compared to a Scott-Marrin reference standard. Percent differences between reference std and in house blend were less than ten percent. Gas components were purchased as a mix from Restek (VOA CYL III) and back calculated from ng/s to ppbv. Freon 114 was obtained from Aldrich as pure and tedlar bag blended to a working ppmv level. Other liquid TO14 compounds were prepared by the static dilution bottle technique<sup>2</sup>. From the working ppmv levels, aliquots were injected into a pre-cleaned evacuated SUMMA canister and then pressurized with humidified nitrogen from the gas side of a liquid nitrogen dewar. Cans were pressurized to approximately 1500 mm Hg (approximately 15 psi) and allowed to equilibrate overnight<sup>3</sup>. Standards were prepared at 50, 10, 1, 0.2, and 0.02 ppbv.

## Calibration

A sample size of 500 cm<sup>3</sup> was used and a five point calibration was performed at 1, 5, 10, 20, and 50 ppbv. (See Figure 1 for TIC of 10 ppbv Standard) Relative standard deviations were less than 10 percent in most cases. Software produces a CLP-like Form 5-Initial Calibration Report seconds after data is processed. Tune reports for BFB are automatically produced after acquisition.

## Mdl Study

The method detection limit was determined by the procedure of Glaser, et al<sup>4</sup>, run an estimated sample at five times the mdl, analyze seven replicates, calculate the mean, standard deviation (SD) and multiply the SD by Student-t value of 3.143. To accurately simulate 0.2 ppbv sample two method detection limit studies were performed: first, a 100 cm<sup>3</sup> sample from a 1.0 ppbv can and analyzed seven times (See Table 1) and second, a sample size of 500 cm<sup>3</sup> from a 0.2 ppbv can and analyzed seven times. (See Table 2.) Benzene contamination occurred in both studies and in the second study, contamination of toluene and the high boilers suggest a dirty can.

Extracted ion chromatograms are provided for the gases at 10 ppbv, 0.2 ppbv, and 20 pptv (see Figure 2) Note actual amounts of gases in figure 2.

## 20 Pptv Study

A 20 pptv was prepared and analyzed with a 500 cm<sup>3</sup> sample size (See Figure 3 for full scan spectra)

To enhance the sensitivity of the MSD a 20 pptv sample was analyzed with the electron multiplier operated at BFB tune plus 400 volts and response improved by a factor of ten with some increases in noise. (See Figure 2 and 3 lower graph)

## CONCLUSIONS

Sensitivity is improved by optimizing the following parameters:

1. Water management allowing direct capillary insertion and polar compound analyses
  2. Cryofocusing and Electronic Pressure Control improving gas chromatographic resolution
  3. Using a low background high sensitivity benchtop quadrupole mass spectrometer
- GC/MS full scan data is attainable at the pptv level. Raising multiplier 400 volts above tune enhances response and accordingly signal to noise ratio. Method detection limits studies performed show detection limits in the 10 to 200 pptv with most compounds in the 10 to 20 range. Reliable quantitation level (RQL) suggested by Eaton<sup>5</sup> put limits at 50 pptv. Improvements in sensitivity call for extremely clean cans. Contamination of common solvents used in an environmental laboratory is a challenge for trace analysis. Cleanliness and control of cans is critical in trace analysis. Larger sample sizes will improve quantitation limits but a larger trap may be needed. A smaller sample size may be used and still exceed CLP SOW CRQLs and EPA TO14.

Quality assurance is available in the system software for immediate feedback on system performance and quality analytical data. Automation of these reports reduce manual hand calculations and facilitates operator productivity.

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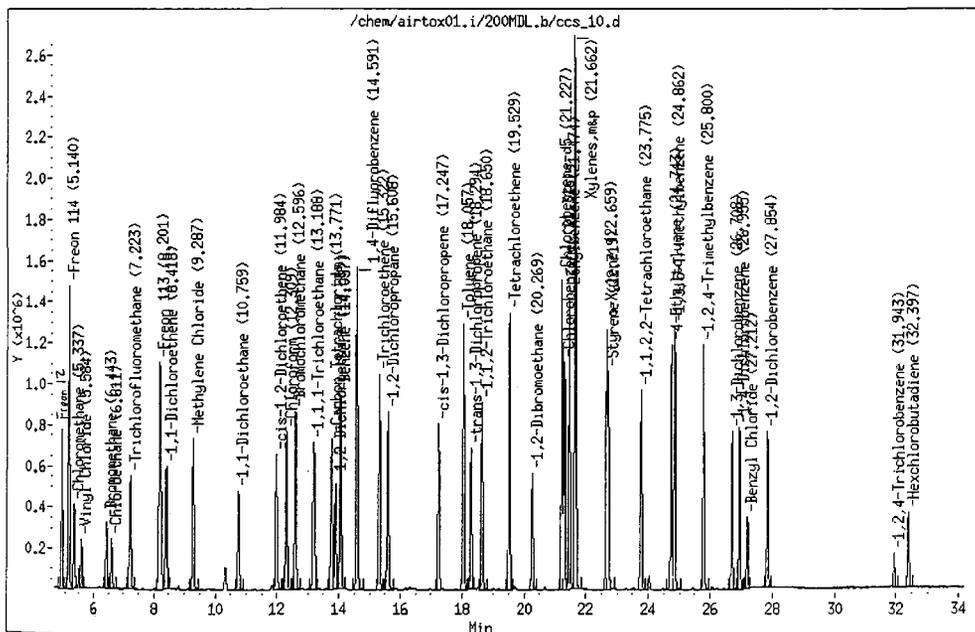


Figure 1. TIC of 10ppbv TO14 STD ( 500cc of 10 ppbv).

**Table 1. Seven Replicates of 100cc of 1.0 ppbv.**

Compound	Methc Exp	MDL1	MDL2	MDL3	MDL4	MDL5	MDL6	MDL7	AVG	%REC	STD	MDL
Blank Conc												
Freon 12	0.00	0.21	0.24	0.25	0.25	0.25	0.24	0.25	0.25	115%	0.00	0.02
Freon 114	0.00	0.21	0.19	0.19	0.20	0.23	0.19	0.23	0.22	98%	0.02	0.06
Chloromethane	0.02	0.52	0.64	0.62	0.62	0.65	0.64	0.62	0.63	119%	0.01	0.04
Vinyl Chloride	0.00	0.47	0.46	0.45	0.45	0.45	0.45	0.47	0.47	96%	0.01	0.03
Bromomethane	0.01	0.15	0.17	0.17	0.17	0.20	0.17	0.16	0.18	111%	0.01	0.04
Chloroethane	0.00	0.39	0.22	0.22	0.22	0.23	0.22	0.23	0.22	57%	0.00	0.02
Trichlorofluoromethane	0.00	0.18	0.20	0.21	0.20	0.21	0.20	0.21	0.20	114%	0.01	0.02
Freon 113	0.00	0.24	0.25	0.26	0.26	0.26	0.25	0.25	0.25	107%	0.01	0.02
1,1-Dichloroethene	0.00	0.25	0.28	0.28	0.28	0.28	0.27	0.28	0.27	112%	0.00	0.02
Methylene Chloride	0.37	0.31	0.75	0.86	0.93	0.96	0.87	0.79	0.79	155%	0.08	0.24
1,1-Dichloroethane	0.00	0.25	0.27	0.28	0.29	0.28	0.29	0.28	0.29	115%	0.01	0.02
cis-1,2-Dichloroethene	0.00	0.25	0.27	0.28	0.28	0.28	0.28	0.27	0.28	112%	0.00	0.02
Chloroform	0.00	0.24	0.28	0.29	0.29	0.29	0.29	0.29	0.29	118%	0.00	0.01
1,1,1-Trichloroethane	0.00	0.24	0.28	0.28	0.28	0.28	0.29	0.28	0.28	120%	0.00	0.01
Carbon Tetrachloride	0.00	0.21	0.24	0.24	0.24	0.24	0.24	0.24	0.24	113%	0.00	0.00
1,2-Dichloroethane	0.01	0.24	0.28	0.29	0.29	0.30	0.29	0.29	0.29	118%	0.01	0.02
Benzene	0.46	0.33	0.75	0.80	0.85	0.83	0.80	0.78	0.80	103%	0.03	0.10
Trichloroethene	0.00	0.24	0.26	0.26	0.25	0.26	0.26	0.26	0.25	106%	0.00	0.02
1,2-Dichloropropane	0.00	0.25	0.27	0.28	0.27	0.27	0.27	0.27	0.27	111%	0.00	0.01
cis-1,3-Dichloropropene	0.00	0.20	0.22	0.23	0.22	0.23	0.23	0.22	0.23	112%	0.01	0.02
Toluene	0.16	0.43	0.54	0.53	0.55	0.55	0.54	0.54	0.54	90%	0.01	0.02
trans-1,3-Dichloropropene	0.01	0.20	0.23	0.23	0.23	0.23	0.23	0.23	0.23	109%	0.00	0.01
1,1,2-Trichloroethane	0.01	0.25	0.27	0.27	0.27	0.27	0.27	0.27	0.27	107%	0.00	0.00
Tetrachloroethene	0.00	0.25	0.26	0.26	0.27	0.27	0.26	0.26	0.26	106%	0.00	0.02
1,2-Dibromoethane	0.01	0.24	0.26	0.26	0.27	0.27	0.27	0.26	0.27	107%	0.01	0.02
Chlorobenzene	0.01	0.26	0.27	0.27	0.28	0.28	0.27	0.27	0.27	105%	0.00	0.02
1,1,2,2-Tetrachloroethane	0.02	0.28	0.32	0.32	0.33	0.32	0.32	0.33	0.32	111%	0.01	0.02
Ethylbenzene	0.03	0.29	0.31	0.31	0.32	0.31	0.31	0.30	0.31	97%	0.01	0.02
Xylenes, m&p	0.13	0.69	0.79	0.81	0.83	0.81	0.81	0.81	0.80	98%	0.01	0.04
o-Xylene	0.05	0.32	0.35	0.36	0.36	0.36	0.36	0.36	0.36	98%	0.00	0.01
Styrene	0.02	0.26	0.26	0.26	0.27	0.26	0.27	0.26	0.27	95%	0.01	0.02
4-Ethyltoluene	0.02	0.31	0.33	0.34	0.35	0.34	0.34	0.33	0.34	102%	0.01	0.02
1,3,5-Trimethylbenzene	0.02	0.31	0.32	0.32	0.32	0.32	0.33	0.32	0.32	99%	0.00	0.01
1,2,4-Trimethylbenzene	0.04	0.32	0.35	0.36	0.37	0.35	0.36	0.36	0.36	99%	0.01	0.02
1,3-Dichlorobenzene	0.04	0.30	0.31	0.32	0.32	0.32	0.33	0.32	0.32	96%	0.01	0.02
1,4-Dichlorobenzene	0.04	0.29	0.31	0.32	0.33	0.32	0.33	0.32	0.33	98%	0.01	0.02
Benzyl Chloride	0.06	0.15	0.19	0.21	0.23	0.19	0.22	0.20	0.22	100%	0.02	0.05
1,2-Dichlorobenzene	0.03	0.29	0.31	0.32	0.33	0.32	0.33	0.33	0.33	103%	0.01	0.02
1,2,4-Trichlorobenzene	0.08	0.25	0.31	0.31	0.34	0.30	0.33	0.32	0.34	97%	0.02	0.05
Hexchlorobutadiene	0.02	0.29	0.34	0.34	0.36	0.33	0.35	0.34	0.35	116%	0.01	0.03

\* Note percent recovery calculated based on average minus method blank divided by expected concentration

Normal Sample Size 500cc

Single Point Calibration at 500 cc of 10 ppbv

0.2 ppbv run a sample size of 100cc at 1 ppbv

**Table 2. Seven Replicates of 500cc of 0.2 ppb.**

Compound	Method	MDL1	MDL2	MDL3	MDL4	MDL5	MDL6	MDL7	STD	MDL
	Blank									
Freon 12	0.00	0.24	0.23	0.23	0.24	0.24	0.23	0.23	0.01	0.02
Freon 114	0.00	0.23	0.23	0.23	0.22	0.23	0.23	0.22	0.00	0.02
Chloromethane	0.02	0.55	0.54	0.55	0.52	0.55	0.51	0.53	0.02	0.05
Vinyl Chloride	0.00	0.50	0.48	0.49	0.50	0.49	0.48	0.47	0.01	0.03
Bromomethane	0.01	0.26	0.28	0.28	0.23	0.28	0.21	0.25	0.03	0.09
Chloroethane	0.00	0.40	0.39	0.38	0.39	0.39	0.40	0.38	0.01	0.03
Trichlorofluoromethane	0.00	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.00	0.00
Freon 113	0.01	0.28	0.27	0.28	0.27	0.28	0.28	0.27	0.01	0.02
1,1-Dichloroethene	0.00	0.29	0.29	0.29	0.29	0.28	0.28	0.27	0.01	0.02
Methylene Chloride	0.50	0.99	0.95	0.93	0.90	0.91	0.92	0.89	0.03	0.11
1,1-Dichloroethane	0.00	0.29	0.29	0.29	0.29	0.29	0.29	0.28	0.00	0.01
cis-1,2-Dichloroethene	0.01	0.29	0.29	0.29	0.29	0.29	0.28	0.28	0.00	0.02
Chloroform	0.00	0.30	0.30	0.30	0.30	0.30	0.30	0.28	0.01	0.02
1,1,1-Trichloroethane	0.02	0.36	0.35	0.36	0.36	0.36	0.35	0.35	0.01	0.02
Carbon Tetrachloride	0.00	0.24	0.25	0.24	0.24	0.25	0.24	0.24	0.00	0.02
1,2-Dichloroethane	0.01	0.31	0.30	0.30	0.31	0.31	0.31	0.30	0.01	0.02
Benzene	0.48	0.39	0.40	0.41	0.46	0.47	0.46	0.44	0.03	0.10
Trichloroethene	0.02	0.30	0.30	0.29	0.30	0.30	0.29	0.28	0.01	0.02
1,2-Dichloropropane	0.02	0.31	0.31	0.30	0.30	0.30	0.30	0.29	0.01	0.02
cis-1,3-Dichloropropene	0.02	0.23	0.23	0.23	0.23	0.24	0.23	0.22	0.01	0.02
Toluene	2.01	0.98	0.95	0.95	0.95	0.95	0.94	0.93	0.02	0.05
trans-1,3-Dichloropropene	0.03	0.20	0.20	0.20	0.21	0.20	0.20	0.19	0.01	0.02
1,1,2-Trichloroethane	0.04	0.29	0.29	0.29	0.30	0.29	0.29	0.29	0.00	0.01
Tetrachloroethene	0.05	0.33	0.32	0.32	0.32	0.31	0.32	0.31	0.01	0.02
1,2-Dibromoethane	0.03	0.26	0.26	0.26	0.27	0.27	0.27	0.26	0.01	0.02
Chlorobenzene	0.07	0.34	0.34	0.33	0.33	0.33	0.33	0.33	0.00	0.02
1,1,2,2-Tetrachloroethane	0.14	0.46	0.43	0.41	0.41	0.41	0.41	0.40	0.02	0.06
Ethylbenzene	0.32	0.45	0.45	0.43	0.43	0.43	0.43	0.43	0.01	0.03
Xylenes,m&p	1.02	1.15	1.14	1.11	1.11	1.09	1.10	1.08	0.03	0.08
o-Xylene	0.36	0.49	0.47	0.45	0.46	0.45	0.45	0.45	0.02	0.05
Styrene	0.17	0.32	0.30	0.29	0.28	0.28	0.29	0.30	0.01	0.04
4-Ethyltoluene	0.32	0.52	0.48	0.45	0.42	0.42	0.43	0.46	0.04	0.11
1,3,5-Trimethylbenzene	0.14	0.50	0.49	0.45	0.44	0.44	0.45	0.46	0.02	0.08
1,2,4-Trimethylbenzene	0.33	0.60	0.56	0.52	0.51	0.52	0.51	0.56	0.03	0.11
1,3-Dichlorobenzene	0.40	0.52	0.47	0.41	0.40	0.40	0.39	0.40	0.05	0.15
1,4-Dichlorobenzene	0.41	0.52	0.46	0.48	0.46	0.45	0.44	0.41	0.03	0.11
Benzyl Chloride	0.39	0.31	0.27	0.22	0.18	0.15	0.13	0.15	0.07	0.21
1,2-Dichlorobenzene	0.30	0.55	0.47	0.44	0.42	0.42	0.42	0.44	0.05	0.15
1,2,4-Trichlorobenzene	0.68	1.14	1.13	1.19	1.25	1.21	1.24	1.16	0.05	0.15
Hexachlorobutadiene	0.15	0.82	0.82	0.87	0.89	0.93	0.95	0.94	0.05	0.17

Normal Sample Size 500cc

Single Point Calibration at 500 cc of 10 ppbv

0.2 ppbv run with sample size of 500cc @0.2 PPBV

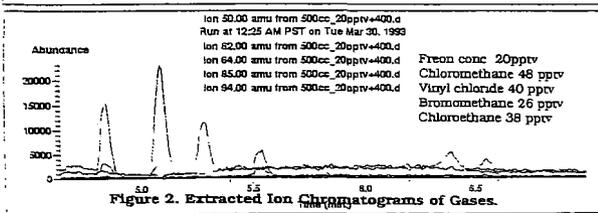
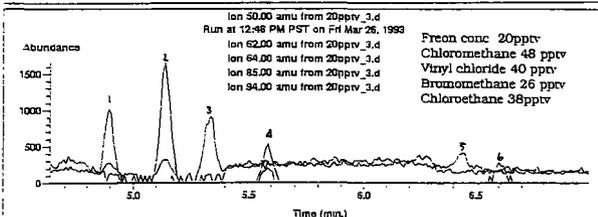
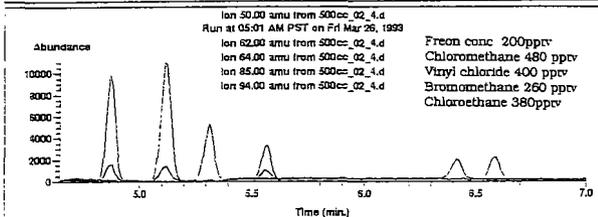
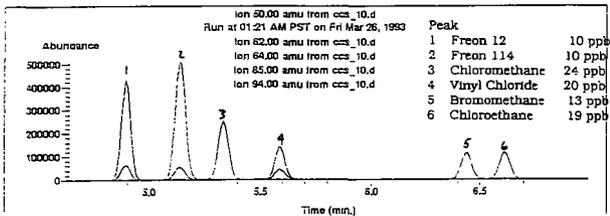


Figure 2. Extracted Ion Chromatograms of Gases.

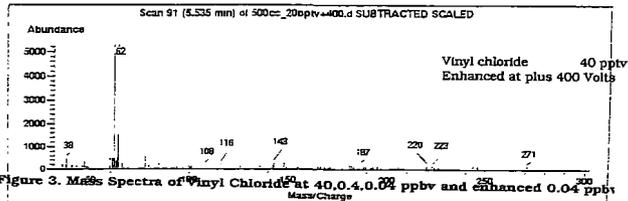
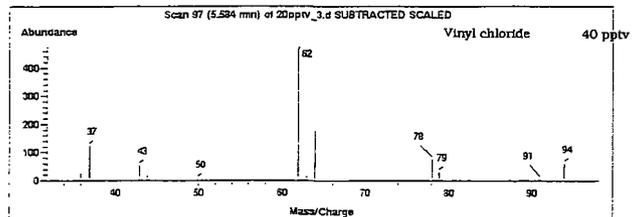
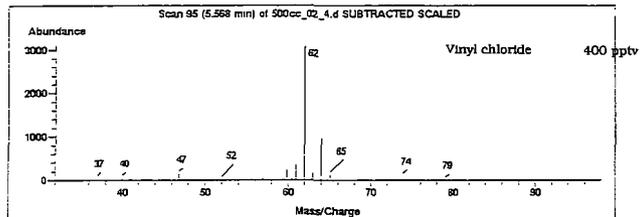
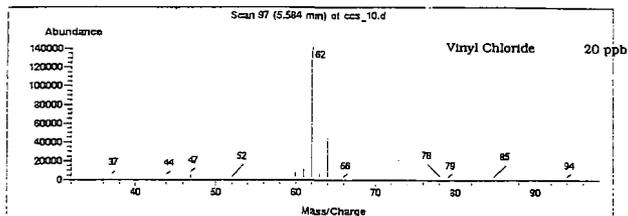


Figure 3. Mass Spectra of Vinyl Chloride at 40, 0.4, 0.02 ppbv and enhanced 0.04 ppbv

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## A SIMPLE, ACCURATE PROCEDURE FOR PREPARATION OF ANALYTICAL STANDARDS FOR TO14 INSTRUMENT CALIBRATION

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### ABSTRACT

Several procedures are currently available for preparation of TO14 Volatile Organic Compounds in humidified zero air or humidified nitrogen at the high ppt - mid ppb range. Diluted standards can be generated directly from the pure (neat) compounds, or by purchasing standard mixes at a vendor or NIST referenced concentration for subsequent transfer into a SUMMA passivated canister. Dynamic dilution can improve the accuracy and precision of standards preparation relative to static dilution by reducing the number of error causing variables. Even initial transfer losses can be ignored in a system that is properly constructed and operated.

A compact, economical dynamic dilution system is presented which simplifies the preparation of ambient air level standards. The system insures a high degree of reproducibility and transfer accuracy by maintaining equilibrium conditions during canister filling operations. Transfer losses are allowed to occur before canister filling (e.g., before equilibrium is achieved) and therefore do not affect the intended concentrations in the canister. Standards can be pressurized into canisters without using a pump, and the relative sample humidity can even be tailored somewhat.

### INTRODUCTION

Calibration standards in the range of 0.5 - 20 ppb are needed for EPA Method TO14 to calibrate the GC/MS and verify proper operation of the combined preconcentrator/GC/MS analytical system. Due to the low concentrations involved, special care must be taken to insure that standards are prepared accurately and without contamination. Several methods are currently being used to prepare these standards, as shown in Table 1. Each of these techniques has its advantages and limitations. For example, any technique using methanol (P&T or direct injection) may change the final matrix enough that obtained response factors are not valid for non-methanol containing matrices, such as ambient air. In this case, transmission through a Nafion dryer (if used) or even recovery or stability in canisters could change significantly when saturated with methanol.

**TABLE 1 - TO14 Standard Preparation Techniques**

- Serial Dilution/Flash Vaporization
  - Dilute into liquid
  - Dilute into gas phase
- Direct injection of Methanol (P&T) Standard
- Purging of P&T Standard from Sparge Vessels
- Loop Injection of Calibrated Mix
- Dynamic Dilution of Calibrated Mix

Other techniques involving quantitative transfers at non-equilibrium conditions (Serial Dilution and Loop Injection) could result in fluctuating analyte concentrations due to interactions with surfaces, especially during gas phase transfers where the matrix ( oxygen, nitrogen, and argon ) has little solvating influence to keep the VOC's off the container or syringe walls.

Dynamic Dilution is unique in that it can be operated fully under equilibrium conditions. It shouldn't matter if analytes are initially adsorbing onto surfaces in the diluter as long as a "mass in = mass out" relationship is established before commencement of canister filling. If this relationship is left undisturbed during the entire canister filling operation, the analyte concentrations should remain constant. The following sections describe a simple implementation of Dynamic/Equilibrium Dilution for preparation of VOC concentrations in the 0.5 - 100 ppb range.

## INSTRUMENTATION

The Entech 4560 Dynamic Dilution System is a 6 channel calibrated standards generator that was designed to operate fully under equilibrium conditions (FIGURE 1). Channel 1 is used to introduce a dilution gas, either humidified nitrogen or zero air, generally at flow rates of 0.5 - 5 liters/min. Depending on the complexity desired for the final diluted standard, up to 5 more channels can be used to introduced calibrated standard mixes containing 0.5 to 40 ppm of each analyte. Both Alphagaz ( Morrisville, PA ) and Scott Specialty Gases ( Plumsteadville, PA ) currently have a single mix at 1-2 ppm that contains 40 of the TO14 analytes. Due to incompatibility and storage problems at ppm levels, however, the 80-90 VOC's that will require monitoring in accordance with the 1990 Clean Air Act Amendment (Title III) will need to be blended from as may as 3-5 high concentration cylinder mixes. The Mass Flow Controllers (MFC's) used for controlling flow rates of standard are usually chosen to be 10-100 sccm (standard cc per minute), depending on the concentration of the high level mixes.

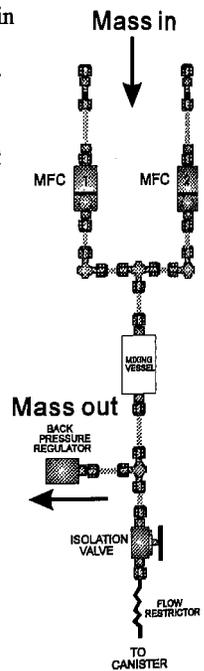


Figure 1

The system operates under equilibrium conditions by maintaining constant flow rate, tem-

perature, and system pressure. Flow rates are regulated by individual mass flow controllers with digital readouts continuously showing setpoint and actual flow rates. Temperatures are at ambient (20-25 deg. C) and shouldn't change more than a few degrees during standards preparation. Pressures are maintained relatively constant by providing back pressure regulation at 25 psig. Before withdrawing standard into a SUMMA canister, the combined flow is passed through a mixing region to insure homogeneity. A low pressure return line is available for equilibrating the line out to the canister itself before standard introduction.

## DISCUSSION

In order to achieve a mass in = mass out condition, a period of about 15 minutes is usually necessary to reach a steady state condition where material is coming off of wetted surfaces as fast as its adsorbing on. Polar and/or heavy VOC's would have the greatest tendency to interact with surfaces and should therefore take the longest to achieve steady state conditions. During canister filling, the dilution manifold should not experience the initial vacuum of the canister, otherwise VOC's on the surfaces could be stripped off, resulting in even higher VOC concentrations than expected. To prevent this, a back pressure regulator is attached to the high pressure exhaust port. A restricter is then placed between the 4560 Diluter and the canisters so that a maximum flow rate of 500 sccm is experienced at the start of canister filling. In general, as long as at least 500 cc/min total flow is maintained through the diluter, at least some flow will go through the back pressure regulator during canister filling thereby maintaining the pressure at 25 psig +3 psig.

Table 1 shows a typical dilution scheme using a 1.0 ppm TO14 standard from Scott Specialty Gases. A 0-5000 and a 0-50 sccm are used for the diluent and the standard mix, respectively. After setting flow rates, the system is given 15 minutes to achieve a mass in = mass out steady state before beginning to fill a canister. Due to the volume of the step down regulator used for the standard cylinder mix and therefore the extended time necessary to purge it with fresh standard, the first canister prepared should be the high concentration standard where the cylinder mix flow rate is at a maximum (50 sccm in this case). Equilibration should then occur in a shorter period of time.

Table 2 shows some polar and non-polar VOC's blended down to 1-50 ppbv and analyzed by GC/MS. All compounds showed less than 10% Relative Standard Deviation, which is nearing the maximum theoretical precision of mass spectrometric detection.

## CONCLUSION

The Entech 4560DDS is a commercially available Dynamic Dilution System designed specifically for preparation of low level TO14 standards. Reproducible generation of standards in the range of 0.5 to 100 ppb is easily accomplished with as little as 2 mass flow controllers when using a calibrated ppm level standard cylinder. Operation under constant temperature, flow, and pressure insures that the concentrations introduced into the canister while filling remain constant.

**TABLE 2- GC/MS Response factors for Dynamically Diluted Polar and Non-Polar VOC's**

Compound	ppb						%RSD
	1	2	5	10	20	50	
Methanol	2.59	2.67	2.83	2.30	2.32	2.41	8.4
1,1- Dichloroethane	.78	.69	.66	.68	.65	.66	7.2
1,1,1- Trichloroethane	2.71	2.30	2.28	2.21	2.15	2.12	9.4
Tetrachloroethylene	.96	.85	.78	.80	.75	.76	9.5
Bromofluorobenzene	.62	.61	.63	.69	.64	.63	4.3
1,3,5- Triethylbenzene	1.35	1.20	1.15	1.42	1.35	1.24	7.9
1,2,4- Trimethylbenzene	2.97	2.78	2.55	2.61	2.48	2.34	8.5

Data Compliments of J. Stanton, Westinghouse WIPP Program, Carlsbad, NM.

**TABLE 3- Typical Dilution of a 1 ppm TO14 Mix**

0-5 L/min		0-50 sccm		Diluted Conc. in ppb
Zero Air in L/min	MFC's % of Max	1 ppm Mix In cc/min	MFC's % of Max	
5.00	100%	5.0	10%	1
2.50	50%	5.0	10%	2
1.99	40%	10	20%	5
1.98	40%	20	40%	10
1.96	39%	40	80%	20
0.95	19%	50	100%	50
0.45	8%	50	100%	100

THE ANALYSIS OF CANISTER SAMPLES IN LOUISIANA  
BY NON-CRYOGENIC CONCENTRATION AND GC/MS ANALYSIS.

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**ABSTRACT**

The analysis of canister samples by EPA Method TO-14 normally relies on the use of a cryogenic trap in order to concentrate pollutants from a sample volume of about 400 ml. However when analyzing samples collected under high humidity conditions, the water vapor collected can cause plugging of the cryogenic trap. A nafion permeable membrane drier can be used to reduce the amount of water vapor collected. This device however can adversely affect the collection of polar compounds and other highly volatile compounds. Additionally, cryogenic concentrators are typically expensive and require large quantities of cryogenic fluid to concentrate the target analytes.

The Louisiana Department of Environmental Quality has modified a sorbent based organic vapor concentrator for the analysis of canister samples collected at five sampling sites around Louisiana. The resulting concentrator and analysis system have been shown to generate excellent analytical results for the compounds of interest. The analysis system consists of a XonTech 930 Organic Vapor Concentrator attached to a Hewlett-Packard 5890 Gas Chromatograph and a 5971 Mass Selective Detector (MSD) operated in the Selective Ion Monitoring (SIM) mode. The QA/QC procedures used in the analytical procedure and the results obtained from the ambient air sampling program will be discussed in this paper.

## INTRODUCTION

The Louisiana Department of Environmental Quality (LDEQ) has conducted ambient air monitoring for air toxics since 1984. Most of that monitoring effort has concentrated upon auto gas chromatograph monitoring stations fitted with Flame Ionization Detectors. While these monitoring stations can provide a great deal of monitoring data they are limited in the number and types of compounds which can be successfully monitored. Since data on many halogenated volatile organic compounds found in the ambient air in Louisiana was limited, a canister based sampling program was initiated.

The analytical system selected for the analysis of these samples was a Hewlett Packard Model 5890 Gas Chromatograph coupled to a HP Model 5971 mass selective detector. Initially the sample concentration system consisted of an adsorbent tube thermal desorber modified to provide cryogenic concentration of the canister samples. This concentration system was plagued with a several problems. Due to the high humidity present in the Louisiana ambient air, the cryogenic trap associated with the concentrator frequently plugged with ice buildup. A number of techniques were employed to remove the water from the sample stream but these procedures adversely affected the recovery of the some of the target analytes. The liquid nitrogen consumption rate with this concentrator system was also very high. Additionally the system could not be automated to analyze multiple samples. Since the financial resources within the department were limited a low cost alternative method was sought.

The auto gas chromatograph monitoring program conducted by the department utilizes a XonTech Model 930 Organic Vapor concentrator which has proven to be very reliable and very cost effective to operate. This sample concentrator utilizes adsorbent traps for sample concentration rather than using cryogenics. A study was therefore initiated to determine if that concentrator system could be coupled to the GC/MS system and modified to provide the automated analysis of canister samples.

## ANALYTICAL PROCEDURES

The XonTech concentrator is fitted with two multi-bed adsorbent traps consisting of Tenax-GR/Carboxen-569/Carbosieve S-III packed in a stainless steel tube (12" length x 1/8" O.D.). The concentrator is programmed to collect the canister samples over a 50 minute period at a flow rate of 5 CC/min for a total sample volume of about 0.25 liters. The sample flow through the adsorbent trap is maintained at a constant rate by a mass flow controller contained within the sample concentrator. The Organic Vapor Concentrator is connected to the Gas Chromatograph by means of a heated transfer line.

At the beginning of each desorption cycle the concentrator sends a remote start signal to the Gas Chromatograph and Computer Data System. The adsorbent trap is heated to 210 C and the sample is thermally desorbed at a flow rate of 4 CC/min directly into the Gas Chromatograph. The capillary column used is a J & W DB-624 75 meter 0.53 mm I.D. with a 3.0 um stationary phase. The gas Chromatograph is temperature programmed for a 6 minute hold at 35 C, then ramped @ 4.5 /min to 180 C. The total analytical run time is 45 minutes. The column is connected to the mass selective detector by means of a capillary splitter which allows only a flow of 1.0 CC/min to enter the ion source. The MSD is programmed to operate in the selective ion

monitoring mode in order to provide maximum sensitivity for the analytes of interest.

#### QUALITY ASSURANCE

The instrument is calibrated at five calibration levels from 0.5 ng/l to 25 ng/l for all of the target compounds. The calibration and internal standard mixtures are prepared in 15 liter Summa® passivated canisters. The humidified calibration mixture is prepared at a concentration of 25 ng/l for each compound. Multiple calibration levels are accomplished by changing the calibration standard sampling time on the concentrator. Table 1 shows how each calibration level is programmed.

( Table 1 )

Calibration Levels Utilized For Calibration Curve

Calibration Level	Concentration	Sample Vol.	Sampling Time
Level 1	25.0 ng/L	250 CC	50 minutes
Level 2	10.0 ng/L	100 CC	20 minutes
Level 3	5.0 ng/L	50 CC	10 minutes
Level 4	1.0 ng/L	10 CC	2 minutes
Level 5	0.5 ng/L	5 CC	1 minute

The resulting calibration curves as illustrated in Figure 1 have been shown to be linear for all of the target compounds with a curve fit of 0.98 or better. The curves also demonstrate the lack of any breakthrough in the adsorbent traps at the higher sampling volumes. The d6-Benzene internal standard and the 4-Bromoflourobenzene mass standard surrogate are automatically injected into every analysis by the concentrator. The peak areas for each of these compounds are recorded and plotted onto control charts.

Spiked canisters are prepared periodically to challenge the analytical system. The precision and accuracy of the analytical method were determined by running a series of sixteen analyses of a spiked canister containing low levels of the target compounds. The results of this analysis showed that the analytical system was able to accurately measure all of the target compounds within an accuracy of +/- 25% and with a precision of +/- 15%.

Several ambient samples were analyzed by a Saturn Air GC/MS system recently purchased by the department and the results shown in Table 3, were compared to the results from the LDEQ canister analysis system. The results show that the two methods of analysis were comparable, with all differences within the standard margin of error.

#### AMBIENT DATA RESULTS

Currently there are six canister sampling sites located around Louisiana. These sites are located in Baton Rouge, Baker, Dutchtown, Shreveport, Monroe and West Lake. The canister samples are collected utilizing XonTech Model 911A samplers. Before sample collection each canister is evacuated and filled with hydrocarbon free air. The canister is then blank analyzed to ensure there is no internal contamination. The canister is re-evacuated and sent out to the sampling site. About 15 liters of ambient air are collected during a single 24 hour sampling period. As a result, the canister is

pressurized to about 20 psig. After sample collection is completed, the canisters are transported back to the laboratory for analysis. Table 2 shows the analytical results of the sampling program From June 1992 through February 1993.

( Table 2 )

Canister Sampling Results  
Mean average concentrations in ppb

	BAK	BTR	DCH	MON	SHV	WSL
Freon-12	1.63	1.92	1.74	1.61	1.89	2.08
Chloromethane	0.73	0.57	0.65	0.57	0.60	0.72
Vinyl chloride	0.02	0.16	0.03	0.00	0.00	0.01
Bromomethane	0.01	0.03	0.01	0.01	0.01	0.01
Chloroethane	0.01	0.09	0.04	0.00	0.04	0.35
Freon-11	0.46	0.56	0.46	0.43	0.46	0.45
1,1-dichloroethene	0.00	0.00	0.01	0.00	0.01	0.00
Acetone	4.10	4.38	2.74	4.21	4.62	5.88
Carbon disulfide	0.10	0.27	0.14	0.25	0.21	0.19
Methylene Chloride	0.15	0.12	0.18	0.07	0.15	0.12
t-1,2-dichloroethene	0.00	0.00	0.01	0.00	0.00	0.00
1,1-dichloroethane	0.00	0.00	0.01	0.00	0.00	0.01
c-1,2-dichloroethene	0.00	0.00	0.00	0.00	0.00	0.00
2-butanone	0.57	0.85	0.68	0.66	1.23	2.15
Chloroform	0.03	0.08	0.03	0.02	0.02	0.05
Methylchloroform	0.15	0.88	0.26	0.18	0.23	0.23
Carbon Tetrachloride	0.16	0.16	0.20	0.13	0.16	0.20
Benzene	1.11	1.65	0.48	0.60	1.13	0.80
1,2-dichloroethane	0.07	0.17	0.11	0.03	0.03	0.10
Trichloroethylene	0.06	0.05	0.06	0.05	0.05	0.10
1,2-dichloropropane	0.00	0.00	0.00	0.00	0.00	0.00
Bromodichloromethane	0.00	0.00	0.00	0.00	0.00	0.00
tl,3-dichloropropene	0.00	0.00	0.00	0.00	0.00	0.00
4-methyl-2-pentanone	0.05	0.08	0.02	0.08	0.08	0.12
Toluene	1.00	1.65	0.65	1.04	1.97	0.81
cl,3-dichloropropene	0.00	0.00	0.00	0.00	0.00	0.00
1,1,2trichloroethane	0.06	0.12	0.01	0.02	0.03	0.42
Perchloroethylene	0.02	0.06	0.05	0.02	0.04	0.06
2-hexanone	0.04	0.04	0.03	0.03	0.06	0.33
Dibromochloromethane	0.00	0.00	0.00	0.00	0.00	0.00
Chlorobenzene	0.02	0.09	0.01	0.01	0.01	0.06
Ethylbenzene	0.16	0.32	0.24	0.26	0.36	0.24
m+p xylene	0.47	1.01	0.43	0.68	0.97	0.49
o xylene	0.14	0.31	0.09	0.22	0.29	0.14
Styrene	0.05	0.08	0.05	0.05	0.05	0.06
Bromoform	0.00	0.00	0.00	0.00	0.00	0.00
Tetrachloroethane	0.01	0.01	0.01	0.01	0.01	0.02

BAK = Baker,  
DCH = Dutchtown

BTR = Baton Rouge  
MON = Monroe

SHV = Shreveport  
WSL = Westlake

It is very apparent from the ambient monitoring data that the orientation of each site to the local point sources is most likely responsible for the differences in concentrations observed between the several sites. The data shows that the sampling sites located in or near urban areas (Baker, Baton Rouge, Shreveport) generally have higher concentrations than those located in more rural areas (Dutchtown, Monroe, Westlake). Since the Baton Rouge site is closer to a major industrial area it would be expected to show higher concentrations. The Baton Rouge site measured the highest levels of Benzene, Vinyl chloride, Methylchloroform, and 1,2-dichloroethane. Except for some slightly higher Freon levels at the Baton Rouge site, all of the sites had about the same measured levels of the common background compounds such as Freon-12, Freon-11, Acetone, trichloroethylene, and Carbon tetrachloride.

### CONCLUSIONS

The results of the study showed that the Organic Vapor Concentrator was able to interface very well with the GC/MS system and produce quality analytical results. The analytical system has proven to be very reliable with low operational cost. An analysis of the analytical results suggests that the system is able to produce data comparable to cryogenic concentration techniques.

Possible alternative applications for this analytical technique would include the use in continuous monitoring stations for air toxics or in mobile laboratories. Without the need for cryogenic coolants this type of system could operate for extended periods of time at remote locations.

( Table 3 )

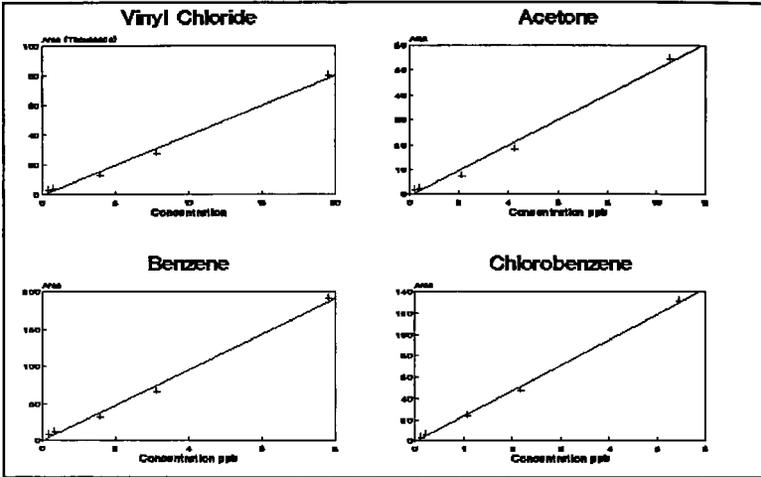
### Comparison of Ambient Sample results

Xontech/Hewlett-Packard System versus a Varian Saturn Air Cryogenic concentration system

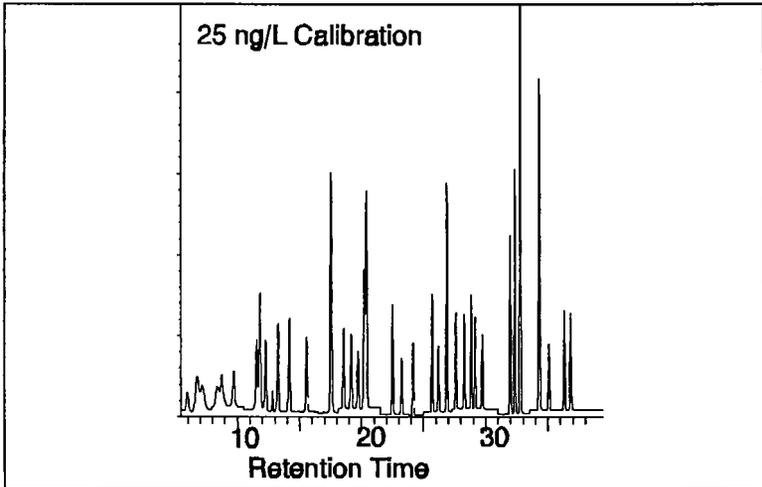
Compound	Sample #1		Sample #2		Sample #3	
	X/HP	Sat.Air	X/HP	Sat.Air	X/HP	Sat.Air
Freon-12	2.31	1.76	2.30	1.41	2.09	1.41
Vinyl Chloride	0.00	0.00	0.02	0.00	0.00	0.00
Carbon disulfide	0.09	0.05	0.07	0.03	0.25	0.12
Chloroform	0.03	0.02	0.03	0.02	0.02	0.01
Methyl Chloroform	0.43	0.30	0.42	0.33	0.30	0.22
Carbon tet.	0.18	0.11	0.17	0.11	0.15	0.11
Benzene	0.54	0.46	0.61	0.50	0.37	0.37
Toluene	0.97	0.67	0.99	0.62	0.33	0.30
1,2-dichloroethane	0.20	0.18	0.00	0.00	0.00	0.00
m+p xylene	0.32	0.38	0.32	0.25	0.17	0.20
o xylene	0.14	0.22	0.14	0.13	0.08	0.11
Styrene	0.04	0.17	0.04	0.09	0.04	0.10
Chlorobenzene	0.01	0.01	0.01	0.01	0.01	0.00

( Figure 1 )

**Example Calibration Curves**



( Figure 2 )



*Session 9*

*Quality Assurance*

Changes to the EPA  
Quality System for the Collection and  
Evaluation of Environmental Data

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Formalized quality assurance (QA) system requirements for the U.S. Environmental Protection Agency (EPA) have been established for more than ten years. During this period, many environmental issues and concerns addressed by the EPA have changed. Other issues, such as hazardous waste clean-up and toxic and related air pollutants, remain a focus of national environmental concern. These environmental issues are bringing changes to the way in which the EPA plans, implements, and assesses its program activities. To meet the needs of the Agency's environmental data collection programs through the end of this century, the QA system of the EPA has been transformed and revitalized.

The EPA QA system provides the necessary management and technical processes to effectively plan, implement, and assess the results of work performed. Within this structure, the program provides managers with "tools" to accomplish each phase of the QA program, including the Data Quality Objectives (DQO) process, Management Systems Reviews (MSRs), and the new Data Quality Assessment (DQA) process.

This paper discusses the current state of the EPA QA system implementation, provides a status report on new QA requirements and guidance documents, and describes some of the new features of the QA program to improve the quality of environmental data operations.

## INTRODUCTION

Since 1984, EPA has been applying quality management principles to the collection, analysis, and use of environmental data. Environmental data help form the basis for nearly all policy, technical, and regulatory actions at EPA. Therefore, it is vital that the collected data are of the type, quantity, and quality needed to make decisions with the desired degree of confidence; that is, to assure management that the data do not lead to an incorrect decision and that the data can withstand scientific and litigative scrutiny. The quality of environmental data may be affected by any aspect of data collection and manipulation, including sampling, analysis, validation of results, and evaluation of the complete measurement system, that may, in turn, impact the decision-making process adversely.

Quality management, in the context of its use by EPA, may be defined as follows:

*Quality Management is that aspect of the overall management systems of an organization that determines and implements policy regarding the Quality System, including strategic planning, allocation of resources, and the planning, implementation, and assessment of programs by the organization.<sup>(1)</sup>*

The EPA commitment to quality is embodied in EPA Order 5360.1<sup>(2)</sup>, which requires all EPA organizations collecting environmental data to implement an effective Quality System.

The presence of quality assurance (QA) and quality control (QC) programs in EPA may be traced back to the early 1970s. By 1979, a formal, Agency-wide QA program was established and the following year, the Quality Assurance Management Staff (QAMS) issued interim guidance for preparing two key QA planning documents, QA Program Plans<sup>(3)</sup> and QA Project Plans.<sup>(4)</sup> These two documents became *de facto* standards and were never updated by EPA for external use, even though revised internal guidance for QA Program Plans was developed in 1986. The need to provide current documentation has become clear.

The environmental programs being undertaken by EPA in 1993 are vastly different from those supported by the QA/QC programs of the 1970s and 1980s. Just as the Agency has evolved to meet changing environmental needs and issues, so must the Agency Quality System change to assure the continuation of having adequate environmental data for decision-making.

## AMERICAN NATIONAL STANDARD FOR ENVIRONMENTAL QUALITY SYSTEMS

Environmental programs are broad in scope and diversity. Over the past twenty years, EPA and other federal, state, and private sector organizations have developed QA/QC programs and requirements that fit their particular mission needs. This practice has created a situation of multiple organizations with different QA/QC requirements, many of which are conflicting in their specific criteria. As a consequence, unnecessary costs have been incurred by government and the private sector to satisfy these duplicative requirements.

For the past three years, QAMS has participated with other federal agencies and private sector companies in an effort led by the American Society for Quality Control to develop an American National Standard for environmental quality systems. This effort has resulted in a proposed standard, ANSI/ASQC E4-1993, Quality Systems Requirements for Environmental

Programs<sup>(5)</sup>, from the ASQC Energy and Environmental Quality Division which is expected to be approved and published by the ASQC and the American National Standards Institute (ANSI) later this summer. EPA has indicated its intention to adopt ANSI/ASQC E4-1993 as the basis for its internal quality system. Moreover, EPA will seek changes to the EPA Acquisition Regulations<sup>(6)</sup> and the EPA Financial Assistance Regulations<sup>(7,8)</sup> to require that organizations satisfy the requirements of ANSI/ASQC E4-1993 as a condition for receiving contract or financial assistance funds.

The impact of ANSI/ASQC E4-1993 on the existing EPA Quality System is not expected to be great since many of the elements of E4 are already found in the Agency Quality System, including the Quality Management Plan (QMP), the Data Quality Objectives (DQO) process, the QA Project Plan (QAPP), the Data Quality Assessment (DQA) process, and the Management Systems Review (MSR). While some terminology has changed, greater consistency will result and unnecessary costs will be reduced.

## NEW AND REVISED DOCUMENTATION

In anticipation of the new standard, QAMS has undertaken a comprehensive development program for new and replacement documentation to implement upgraded E4-based quality systems across the Agency. Two kinds of documents are planned: requirements documents and guidance documents. As the name suggests, *requirements documents* will define mandatory criteria. These documents and a revised EPA Order on quality management will be incorporated into a *Quality Manual* for internal use, and will be issued as an EPA policy document following Agency-wide review and concurrence later this year. The requirements documents will be issued separately for use outside the Agency by contractors and financial assistance recipients. The *guidance documents* are non-mandatory and will be issued for general use both internally and externally.

The availability of the new requirements and guidance documents will commence in a few months and continue for another 18-24 months. The following is a summary of some of the documents that are being developed currently:

EPA QA/R-1      EPA Quality Systems Requirements for Environmental Programs

QA/R-1 is the policy document by which EPA will implement the proposed American National Standard ANSI/ASQC E4, when the standard has been approved. The draft is complete. It also contains the requirements for the QA Annual Report and Work Plan (QAARWP). Availability is expected in fall 1993.

EPA QA/G-1      Guidance for Developing, Implementing, and Evaluating Quality Systems for Environmental Data Operations

QA/G-1 provides non-mandatory guidance to help organizations develop a quality system that will meet EPA expectations and requirements. Availability is expected by early 1994.

EPA QA/R-2      EPA Requirements for Quality Management Plans

QA/R-2 is the policy document containing the requirements for the Quality Management

Plan (QMP). An interim draft was issued in August 1992 to "product test" the approach. Since QA/R-2 follows ANSI/ASQC E4, it will not be finalized until the standard has been approved. QA/R-2 is the intended replacement for QAMS-004/80 and the subsequent internal EPA guidance on QA Program Plans issued in 1987. Availability is expected by fall 1993.

EPA QA/R-2A      EPA Requirements for Quality Management Plans for Analytical Laboratories and Facilities

QA/R-2A will provide detailed requirements for environmental analytical labs. Since there may be a national consensus standard for labs, the content of this document is unclear at present. This is a planned item.

EPA QA/G-2      Guidance for Preparing, Reviewing, and Implementing Quality Management Plans

QA/G-2 provides non-mandatory guidance to help organizations develop Quality Management Plans (QMPs) that will meet EPA expectations and requirements. The document will contain tips, advice, and case studies to help users develop an improved QMP. Target Availability is expected by early 1994.

EPA QA/G-3      Guidance for Preparing, Conducting, and Reporting the Results of Management Systems Reviews

QA/G-3 provides non-mandatory guidance to help organizations plan, implement, and evaluate management assessments of their quality systems. The guidance will present a step-by-step description of the MSR process. Availability is expected by late summer 1993.

EPA QA/G-4      Guidance for Planning for Data Collection in Support of Environmental Decision Making Using the Data Quality Objectives Process

QA/G-4 provides non-mandatory guidance to help organizations plan, implement, and evaluate the Data Quality Objectives (DQO) process, with a focus on environmental decision-making for regulatory and enforcement decisions. The guidance will present a step-by-step description of the DQO process. Availability is expected in summer 1993.

EPA QA/G-4A      Guidance for Planning for Environmental Research Using the Data Quality Objectives Process

QA/G-4A provides non-mandatory guidance to help organizations plan, implement, and evaluate the Data Quality Objectives (DQO) process, with a focus on environmental research decision-making. The guidance will present a step-by-step description of the DQO process as applied to R&D programs. Availability is expected by fall 1993.

EPA QA/R-5      EPA Requirements for Quality Assurance Project Plans

QA/R-5 is the intended replacement for QAMS-005/80. This policy document will establish the requirements for QA Project Plans prepared for activities conducted by or funded by EPA. A revised draft was submitted to the Work Group in January 1993 for final review. Comments have been received and are being addressed. Closure on the document will be

reached by early summer. An *interim draft final* version will be made available while the document undergoes Agency "Green Border" review. Availability of the final document is expected in the fall 1993.

**EPA QA/G-5            Guidance for Preparing, Reviewing, and Implementing Quality Assurance Project Plans for Environmental Programs**

QA/G-5 provides non-mandatory guidance to help organizations develop Quality Assurance Project Plans (QAPPs) that will meet EPA expectations and requirements. The document will contain tips, advice, and case studies to help users develop improved QAPPs. Availability is expected by early 1994.

**EPA QA/G-8            Guidance for Preparing, Conducting, and Responding to Technical Assessments for Environmental Data Operations**

QA/G-8 will provide non-mandatory guidance to help organizations plan, conduct, evaluate, and document technical assessments for their programs. Such technical assessments include the Technical Systems Audit (TSA), surveillance, readiness reviews, and the Performance Evaluation (PE). The document will contain tips, advice, and case studies to help users develop improved processes for conducting technical assessments. This is currently a planned item. QAMS expects to use a Work Group process to develop this guidance.

**EPA QA/G-9            Guidance for Environmental Data Quality Assessment: Managing the Process**

QA/G-9 provides non-mandatory guidance for planning, implementing, and evaluating retrospective assessments of the quality of the results from environmental data operations. DQA is a statistically-based, quantitative evaluation of the extent to which a data set satisfies the user's needs (or DQOs). This particular document is aimed at the project managers who are responsible for conducting the environmental data operations and assessing the usability of the results. The draft is currently undergoing internal review by QAMS. Availability is expected by late summer 1993.

## SUMMARY

The EPA Quality System is changing to meet the needs of the Agency's changing mission and priorities. The adoption of the American National Standard ANSI/ASQC E4-1993 will provide national consistency not only within EPA, but also on a voluntary basis with other federal and state agencies and across the regulated community. The new quality management documents will provide current criteria and guidance for planning, implementing, and assessing quality systems more effectively. They will ensure that environmental programs produce the type and quality of environmental data needed for key decisions.

## REFERENCES

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3. "Interim Guidelines and Specifications for Preparing Quality Assurance Program Documentation," U.S. Environmental Protection Agency, QAMS-004/80 (December 1980).
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6. "Subpart 1546.2 - Contract Quality Requirements," U.S. Environmental Protection Agency, EPA Acquisition Regulations, Title 48 Code of Federal Regulations, Chapter 15 (October 1988).
7. "Part 30 - General Regulation for Assistance Programs for Other than State and Local Governments," U.S. Environmental Protection Agency, Title 40 Code of Federal Regulations, Chapter 1 (July 1990).
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The National Performance Audit Program (NPAP)

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**ABSTRACT**

The National Performance Audit Program (NPAP) is one of the major components in the quality assurance of the Nation's air monitoring program. Over the last several years and especially in 1993, the NPAP has undergone a metamorphosis. This paper will explore some of the forces behind this change as well as the resulting changes which include expansion of the NPAP to cover all the criteria pollutants, new audit equipment design, more audit equipment, more sites audited, and changes in the audit site selection process. The paper will include a review of the audit equipment used throughout the program's existence, an examination, pollutant by pollutant, of the number of audits performed each year beginning in 1989, and other enhancements of the expanded NPAP.

**Disclaimer**

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**INTRODUCTION**

The Nation's ambient air monitoring program contains monitors for the six pollutants that have national ambient air quality standards (NAAQS). These pollutants are carbon monoxide (CO), lead (Pb), nitrogen dioxide (NO<sub>2</sub>), ozone (O<sub>3</sub>), particulate matter smaller than 10 microns (PM-10), and sulfur dioxide (SO<sub>2</sub>). The pollutants and associated standards are shown in Table 1.

Table 1. National ambient air quality standards.

Pollutant	Primary standard (health related)		Secondary standard (welfare related)	
	Type of average	Std. level conc.*	Type of average	Std. level conc.
CO	8-hr <sup>b</sup>	9 ppm (10 mg/m <sup>3</sup> )	No secondary standard	
	1-hr <sup>b</sup>	35 ppm (40 mg/m <sup>3</sup> )	No secondary standard	
Pb	Maximum quarterly average	1.5 µg/m <sup>3</sup>	Same as primary standard	
NO <sub>2</sub>	Annual arithmetic mean	0.053 ppm (100 µg/m <sup>3</sup> )	Same as primary standard	
O <sub>3</sub>	Maximum daily 1-hr average <sup>c</sup>	0.12 ppm (225 µg/m <sup>3</sup> )	Same as primary standard	
PM-10	Annual arithmetic mean <sup>d</sup>	50 µg/m <sup>3</sup>	Same as primary standard	
	24-hr <sup>d</sup>	150 µg/m <sup>3</sup>	Same as primary standard	
SO <sub>2</sub>	Annual arithmetic mean	80 µg/m <sup>3</sup> (0.03 ppm)	3-hr <sup>b</sup>	1300 µg/m <sup>3</sup> (0.50 ppm)
	24-hr <sup>b</sup>	365 µg/m <sup>3</sup>		

\*Parenthetical value is an approximately equivalent concentration.

<sup>b</sup>Not to be exceeded more than once per year.

<sup>c</sup>The standard is attained when the expected number of days per calendar year with maximum hourly average concentrations above 0.12 ppm is equal to or less than 1, as determined according to Appendix H of the Ozone NAAQS.

<sup>d</sup>Particulate standards use PM-10 (particles less than 10 micrograms in diameter) as the indicator pollutant. The annual standard is attained when the expected annual arithmetic mean concentration is less than or equal to 50 µg/m<sup>3</sup>; the 24-hour standard is attained when the expected number of days per calendar year above 150 µg/m<sup>3</sup> is equal to or less than 1, as determined according to Appendix K of the PM NAAQS.

There are approximately 4,682 air pollution monitors in the ambient air network. These monitors comprise the State and Local Air Monitoring Stations (SLAMS), the National Air Monitoring Stations (NAMS), and the Prevention of Significant Deterioration (PSD) sites. The distribution of monitors by pollutant is: SO<sub>2</sub>, 613; CO, 497; NO<sub>2</sub>, 312; O<sub>3</sub>, 822; Pb, 426; PM-10, 1359; and total suspended particulate (TSP) matter (old standards), 653.

The quality assurance/quality control of these monitors has three major components: the EPA Regional Office Systems Audits; the Precision and Accuracy Reporting System (formerly PARS); and the National Performance Audit Program (NPAP). The NPAP is a cooperative effort between EPA's Atmospheric Research and Exposure Assessment Laboratory (AREAL), the 10 EPA Regional Offices, and the 170 state and local agencies that operate the SLAMS/NAMS air pollution monitors. Also included in the NPAP are organizations that operate air monitors at PSD sites. Participation in the NPAP is required for agencies operating SLAMS/NAMS and PSD monitors as per Section 2.4 of 40 CFR Part 58, Appendix A and Section 2.4 of 40 CFR Part 58, Appendix B. The NPAP is operated by the Quality Assurance Support Branch of AREAL.

#### AUDITS

The NPAP's goal is to provide audit materials and devices that will enable EPA to assess the proficiency of agencies that are operating monitors in the SLAMS/NAMS and PSD networks. To accomplish this, the NPAP has established acceptable limits or performance criteria, based on SLAMS/NAMS and PSD requirements, for each of the audit materials and devices provided in the program. Any device or material not meeting these predetermined criteria is not used in the program.

All audit devices and materials used in the NPAP are certified as to their true value, and that certification is traceable to a NIST standard material or device wherever possible. The audit materials used in the NPAP are as representative and comparable as possible to the calibration materials and actual air samples used and/or collected in the SLAMS/NAMS and PSD networks. The audit material/gas cylinder ranges used in the NPAP are specified in the Federal Register (Table 2).

Table 2. NPAP audit material/gas cylinder concentration ranges.

	<u>Audit level</u>	<u>Concentration range, ppm<sup>1</sup></u>
SO <sub>2</sub> , O <sub>3</sub> , and NO <sub>2</sub>	1	0.03-0.08
	2	0.15-0.20
	3	0.35-0.45
CO	1	3-8
	2	15-20
	3	35-45
	<u>Audit level</u>	<u>Concentration range, µg/strip<sup>1</sup></u>
Pb	1	100-300
	2	600-1000

<sup>1</sup>Federal Register, 40 CFR Part 58, Appendix A, revised July 1, 1987.

The objectives for the NPAP audits are two-fold: (1) to complete at least 95% of the scheduled audits by the end of the year, and (2) to determine if the participants' performance exceeds the limits shown below.

<u>Audit</u>	<u>EPA determined limits</u>
High volume/PM-10 (SSI)	% difference > ± 15% for 1 or more flows
Dichot (PM-10)	% difference > ± 15% for 1 or more flows
Pb	% difference > ± 15% for 1 or more levels
SO <sub>2</sub> , NO <sub>2</sub> , O <sub>3</sub> , and CO	Mean absolute % difference > 15%

The number of NPAP audits performed from 1989 to the present are shown in Table 3.

Table 3. NPAP audits 1989 to 1993.

Pollutant		Number of NPAP Audits				
		1989	1990	1991	1992	1993*
CO	Labs	129	137	114	134	154
	Samplers	355	345	183	261	357
SO <sub>2</sub>	Labs	135	139	123	142	167
	Samplers	383	238	204	279	355
NO part of NO <sub>2</sub>	Labs	53	59	83	101	122
	Samplers	98	88	119	170	221
NO <sub>2</sub>	Labs	53	59	14	14	122
	Samplers	98	88	19	27	221
O <sub>3</sub>	Labs	14	79	43	135	171
	Samplers	39	142	77	340	482
SSI/hi-vol	Labs	289	293	315	308	350
	Samplers	1938	772	612	1087	1363
Dichot (PM-10)	Labs	13	24	9	12	19
	Samplers	30	44	17	24	54
Pb	Audits	367	297	322	335	404

\*Audits scheduled.

In 1992 100% of the scheduled audits were completed with the exception of NO<sub>2</sub> (15%), O<sub>3</sub> (93%), and dichot (PM-10) (66%). These 3 audits had some equipment problems that are discussed in the following section.

The percentage of 1992 NPAP participants whose performance fell within the EPA guidelines of 15% of the true values was: CO, 94%; SO<sub>2</sub>, 89%; NO, 94%; NO<sub>2</sub>, 79%; O<sub>3</sub>, 97%; hi-vol/PM-10 (SSI), 91%; dichot (PM-10), 65%; and Pb, 92%. These percentages have remained similar since 1989 for SO<sub>2</sub>, NO<sub>2</sub>, and Pb. O<sub>3</sub> (85% to 97%) and NO (81% to 94%) have increased substantially. CO (98% to 94%) and hi-vol/PM-10 (SSI) (94% to 91%) have decreased slightly.

#### NPAP AUDIT EQUIPMENT

##### Ozone

O<sub>3</sub> was added to the NPAP in 1989. The audit device is self-contained with its own zero-air and ozone generation system. At the present time, this system is not as field worthy as desired. The equipment is being modified in an attempt to eliminate downtime due to damages incurred in shipping.

##### High-Vol/PM-10 (SSI)

The reference flow device (ReF) consists of a modified orifice, a wind deflector, a manometer, and five resistance plates. The ReF for the PM-10 (SSI) flow audit is similar except a filter is used as the only flow restrictor.

##### Dichotomous (PM-10)

The NAAQS for particulates changed from TSP to PM-10 in 1987; the dichotomous (dichot) audit device was added to the NPAP in 1989. The original audit equipment included an electronic manometer which was too fragile for repeated shipping. The audit was suspended in 1991 until new audit equipment could be developed. The audits resumed in May 1992. The improved dichot audit device consists of an inclined manometer filled with red gauge oil, an altimeter that measures barometric pressure in millibars, a small dial thermometer that reads in °F, and the laminar flow element (LFE) with an air filter on its inlet. The dichot audit device measures fine flow (15.00 lpm) and total flow (16.7 lpm).

#### Lead (analysis)

The samples are 1.9 cm wide and 20 cm long glass fiber filter strips that have been spiked with an aqueous solution of lead nitrate and oven-dried. Two filter strips comprise a sample.

#### SO<sub>2</sub>/NO-NO<sub>x</sub>/CO (gas dilution system)

CO was added to the NPAP in the mid-70's. The original CO audit materials consisted of a mixture of CO, CO<sub>2</sub>, methane, and zero air in returnable, 150 ft<sup>3</sup> pressurized gas cylinders that simulated ambient air samples. Three cylinders, representing high, medium, and low concentrations, comprised the set. Due to the high cost of shipping the cylinders, demurrage charges and lost cylinders (\$60K per audit), the NPAP began using disposable cylinders in 1985. The use of disposable cylinders reduced the costs of the audit by \$45K per audit.

SO<sub>2</sub> was added to the NPAP in 1981. From 1981 through 1988, the SO<sub>2</sub> materials consisted of an audit device and a compressed gas cylinder containing SO<sub>2</sub> in nitrogen along with a Size A compressed gas cylinder for zero-air. The zero-air cylinder was very expensive (\$50) and was usually good for only one audit. In 1989 the NPAP began using a portable zero-air system to serve as the dilution air source.

NO-NO<sub>x</sub> was added to the NPAP in 1989. At that time, the audit was done using a gas phase titration system.

Beginning in 1991, one gas dilution system was used for all three audits. The system consisted of an audit device, one zero-air system, and two cylinders of gas (NO<sub>x</sub> and a blend of SO<sub>2</sub>, NO, and CO). The EPA went to the gas dilution system to obtain better results and to save money. Unfortunately, the NO<sub>x</sub> would not remain stable in the cylinder, which caused a problem with the NO<sub>x</sub> audits. In 1992 EPA/AREAL scientists combined a Thermo Environmental Instruments Model 165 ozone calibrator with an EPA-designed gas phase titration and capillary dilution system to produce an auditing device potentially applicable to all SLAMS gaseous pollutants. When field and laboratory tests confirmed that this prototype system could be used to audit SO<sub>2</sub>, NO<sub>x</sub>, CO, and O<sub>3</sub> monitors, EPA procured 22 additional devices through the competitive procurement process. These 22 devices arrived in April 1993 and will be used in a pilot program during the summer and fall of 1993 with the goal of introducing them into the NPAP in January 1994.

#### **SITE SELECTION**

Historically, the state and local agencies have been allowed to select the NPAP sites to be audited. The 1989 General Accounting Office (GAO) audit raised concerns about the NPAP site selection process. EPA, henceforth, conducted a review in 1991 that determined the site selection process used had not biased the audit results. EPA additionally responded to the GAO comments by developing site selection criteria (Table 4) that were incorporated into the 1993 NPAP. Priority 1 site selection criteria should be audited annually; priority 2 at least once every 2 years; priority 3 at least once every 3 years; priority 4 at least once every 4 years. All other sites should be audited at least once every 5 years. Based on this criteria, EPA now selects specific sites that are to be audited in the NPAP. The criteria are reviewed annually, and site selection is updated accordingly.

#### **CONCLUSIONS**

The cornerstone of any data collection system is the quality assurance component. The data utilization resulting from the Nation's air monitoring network continues to increase in importance. The strategies developed from the information can cost millions of dollars. Henceforth, we must remain vigilant in our efforts to maintain the integrity of this important data set. In these efforts, the NPAP continues to be refined. The NPAP has expanded to include all the criteria pollutants. The associated instruments and equipment have been improved to incorporate the latest technologies. The NPAP continues to respond to comments from the GAO audits as well as state and local agency contacts. With the increased interest in the data from the Nation's air monitoring community, it was inevitable that the site selection process would also be modified. These modifications were incorporated into the 1993 NPAP.

In summary, the NPAP has expanded to include all criteria pollutants, improved the associated equipment and instruments, and changed its site selection process.

Table 4. Site selection criteria for the NPAP.

Pollutant	Priority	Criteria
O <sub>3</sub>	1	Sites that had expected exceedances of the O <sub>3</sub> NAAQS $\geq$ 1.1 days from 1989 through 1991.
PM-10	2	Sites recording values > the 24-hr. NAAQS.
	3	Sites recording values > 80% but < 100% of the 24-hr NAAQS.
	4	Sites recording values > 50% but $\leq$ to 80% of the 24-hr NAAQS.
CO	3	Sites recording exceedances of the CO NAAQS from 1990-1991.
	3	Some selected sites within CO nonattainment areas.
	4	Sites recording CO values between 7.5 ppm and 9.4 ppm.
Pb	1	Sites located near sources which are subject to potential regulatory compliance, out of compliance, and/or subject to a consent decree.
	2	Sites located near sources that are either in compliance with no violations, are closed for business, or are well above the Pb NAAQS with no significantly questionable data.
SO <sub>2</sub>	2	Sites recording values > the 24-hr SO <sub>2</sub> NAAQS.
	3	Sites recording values between 80% and 100% of the 24-hr SO <sub>2</sub> NAAQS.
	4	Sites recording values > 50% but < 80% of the 24-hr SO <sub>2</sub> NAAQS.
NO <sub>2</sub>	3	Sites recording values > 50% of the annual NO <sub>2</sub> NAAQS

Two New Gas Standards Programs  
At the National Institute of  
Standards and Technology

by

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**ABSTRACT**

The EPA/NIST certified reference materials (CRM) program is being terminated and replaced with two new ones: the NIST Traceable Reference Materials (NTRM) and the Research Gas Mixture (RGM) programs. These new programs are being implemented to provide NIST traceability to a wider number of gas mixtures. The NTRM program will differ from the CRM program in two significant ways: candidate gas mixtures will not have to be identical to a NIST Standard Reference Material (SRM), and the producer of the NTRM rather than EPA will pay NIST to check the concentration of the gas mixture. In the RGM program, NIST will enter into agreements with either governmental, commercial or private organizations to produce gas mixtures for which there are no SRMs or which lie outside the concentration range of existing SRMs. The details of these programs are presented in this paper.

## INTRODUCTION

Many EPA ambient air, stationary source and mobile source regulations mandate the use of gaseous concentration standards traceable to the National Institute of Standards and Technology (NIST) for calibrating the pollutant measurement systems<sup>(1)</sup>. Standard Reference Materials, (SRMs), which are certified and sold by the NIST are the highest quality, NIST-traceable standards available. Presently, NIST supplies SRMs for the following pollutant gases regulated by the EPA: NO, NO<sub>2</sub>, SO<sub>2</sub>, CO, CO<sub>2</sub>, O<sub>2</sub>, and H<sub>2</sub>S.

The above SRMs were developed by the NIST in cooperation with the EPA. In anticipation that the NIST alone could not meet the demand for NIST-traceable standards, EPA and NIST implemented two other mechanisms to meet this demand. These mechanisms, the Protocol Gas program and the Certified Reference Materials (CRM) program were begun to allow the specialty gas industry to provide gas standards traceable to NIST SRMs at costs less than those for SRMs. The Protocol Gas program<sup>(2)</sup> has been quite successful. It is targeted principally to those who use specialty gas mixtures to calibrate air pollutant monitoring systems, whereas the SRM and CRM programs are targeted for use by the specialty gas industry. Protocol Gases cost 10 to 25% of the corresponding SRM, are certified as stable for periods close to or equal to those of the corresponding SRMs and are made to order by the specialty gas industry.

In contrast, the CRM program<sup>(3)</sup> has not achieved its intended purpose, most likely because CRMs are very close in quality and other characteristics to SRMs. As shown in Table 1, for the cost of a CRM, the potential CRM purchaser can have an SRM, a higher quality standard with a longer stability period. Also, suppliers of specialty gases are reluctant to prepare CRMs because the lead time required means they have to prepare each CRM batch on speculation that they can sell and/or use them quickly after the CRM batch is certified. They cannot make only the number of CRMs needed to meet their internal needs, e.g. for calibration and QC standards, because public funds are used to spot-check the supplier's assay of the CRM batch. Thus, EPA requires suppliers of CRMs to make a sufficient number of cylinders in each CRM batch to be able to sell some of them to others, including competitors in the specialty gas industry.

## NTRM AND RGM PROGRAMS

The CRM program is now being replaced by the NIST Traceable Reference Materials (NTRM) program, which, NIST and EPA, hope will correct the deficiencies in the CRM program. NTRMs will differ from CRMs in the following ways:

1. The NTRM concentration can be at or between those of

- SRMs for the same analyte and balance gas.
2. NIST rather than EPA, will spot-check the assay of the NTRM batch.
  3. NIST will assign the analyte concentration(s) to the NTRM.
  4. The supplier of the NTRM will pay NIST for the spot-check of assay.
  5. The NTRM will not have to be sold to others since no public funds are used in the certification.

Table 2 provides a fuller comparison of the NTRM and CRM programs.

But, what if an organization needs a high quality gas standard where either (1) the analyte is the same as an SRM but where the concentration is outside the range of the existing SRMs or (2) the analyte(s) and/or the balance gas are different from an SRM? The NIST and the EPA are implementing the Research Gas Mixture (RGM) program to address these situations. Under the RGM program, the NIST will enter into an agreement with another party, such as a government agency, a trade organization or a specialty gas company, to produce gas mixtures that have different analytes, different balance gases or concentrations outside the range of available SRMs. Since the requesting organization will fund the work, the RGM will be the property of the sponsor but any primary standards developed will be the property of the NIST.

Key features of the RGM program are:

1. Applicable to gas mixtures not covered by the SRM or NTRM programs.
2. Gas mixture likely can be made.
3. Requestor contacts NIST to discuss procedures and development costs.
4. Work statement, schedule, milestones, and deliverables are specified in written agreement with NIST.
5. Requestor funds project up front to amount agreed upon with NIST.
6. NIST develops new or extends current primary standards required to perform the analysis of the candidate RGM.
7. NIST analyzes primary standards suite for precision and accuracy.
8. NIST analyzes candidate RGM to determine analyte concentration(s) and also the levels of impurities of interest.
9. If successful, gas mixtures produced are "NIST traceable" and NIST provides the requestor with a Report of Analyses and a defined period for which the assigned analyte value(s) are valid.
10. Requestor takes possession of all gas mixtures in the RGM batch.

NIST and EPA are now preparing documents that will describe in detail the mechanics of the NTRM and the RGM programs. At this time, some key features of both programs are not firm. One of these is the question of "Exclusivity", that is, what rights will the organization paying for the development of an RGM have to the exclusive use of the NIST primary standards developed as part of the work? For example, should they have exclusive use forever, for 24 months, etc.? If Company B is willing to pay the NIST to develop similar or identical primary standards to those developed for Company A, can or should the NIST do this? If many companies ask the NIST to develop RGMs similar to those developed for Company A, such that development of an SRM is warranted, can the NIST develop the SRM? If EPA decides to regulate a pollutant covered by an RGM, does the NIST have a responsibility to develop an SRM even if it means the owner of the RGM loses market share?

Two other areas where details are not yet firm are:

1. If the first attempt to develop an RGM fails, but the information obtained allows NIST to develop that RGM for someone else, does the first organization have any rights to the RGM?
2. What should the defined period of stability be for each RGM and NTRM and how should the stability be monitored?

None of these questions is easy to answer; in the end, they probably will be decided on a case by case basis.

#### Disclaimer

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Table 1. Comparison between SRMs and CRMs

Parameter	SRM	CRM
Minimum Batch Size	20	10
Cost Each	\$800 - \$1500	\$800 - \$1500
Gas Volume	30 cu. ft.	150 cu. ft.
Analyte Concentration	NIST's choice	Must be within $\pm 1\%$ of SRMs
Balance Gas	NIST's choice	Must be same as SRM
Analyte Assayed Using	NIST Primary Standards	SRMs
Assay Done by	NIST	Supplier of CRM with EPA spot-check assays.
Uncertainty in Assay	$\pm 1\%$	Up to $\pm 2\%$
Assay Valid For	24 48 months	12 - 24 months
Assay Certification Period Begins	When SRM sold	When CRM Batch is certified
Time From Preparation to Availability	18 36 months	6 12 months

Table 2. Comparison between NTRM and CRM programs

CRM	NTRM
Company decides needs	Same
Company prepares mixtures	Company contacts NIST; after agreement, mixtures made
Company performs analyses	Same
Data sent to EPA	Data sent to NIST
EPA selects two cylinders for analysis	NIST selects cylinders for analysis
Cylinders analyzed by EPA	Cylinders analyzed at NIST
All data sent to NIST	Same
Audit lab concurs with concentration	NIST assigns concentration
Audit costs covered by EPA	Costs covered by producer (\$4500 \$6000)
Company provides assay certificate	NIST provides assay certificate
Company distributes mixtures	Same
Company responsible for stability	Same

A Low Cost Procedure to Make Gaseous  
Pollutant Audit Materials

by

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ABSTRACT

EPA has identified over 130 organic and 20 inorganic gases that it is now regulating or plans to regulate as air pollutants. These compounds are covered by a variety of environmental regulations such as RCRA, NSPS, NAAQS, TSCA, NESHAPS, and CERCLA. These compounds can be found in the air from 1 ppb to the 1000 ppm range and in different relative ratios. A gas transfer system is described in this presentation that will allow an organization to prepare a wide variety of QC and QA materials for these gases using a small number of stock gases in compressed gas cylinders. The experiments conducted to characterize the performance of this system to date and the additional experiments planned are described.

Disclaimer

The information in this document has been funded wholly by the United States Environmental Protection Agency. It has been subjected to Agency review and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

## INTRODUCTION

Since the mid-70's, the Atmospheric Research and Exposure Assessment Laboratory (AREAL) of the U.S. Environmental Protection Agency (EPA), Research Triangle Park, NC, has worked with the National Institute of Standards and Technology (NIST) and with the specialty gas industry to develop stable, accurately-certified compressed gas reference materials. After the NIST or a specialty gas company completes short term (i.e., 3 to 12 months) stability tests on candidate reference materials, AREAL takes possession of those that appear stable and subjects them to longer term (i.e., 1 to ten years) stability testing. When not undergoing stability checks, AREAL makes the materials available, free-of-charge, to other organizations to use in developing, validating, calibrating and quality assuring air pollutant measurement systems applicable to such EPA regulations as the RCRA, CERCLA, NSPS, NESHAPS, NAAQS and TSCA.

In 1990, AREAL's inventory contained approximately 500 gas mixtures, and it met both AREAL's needs (for a statistically sufficient number of gas mixtures for its stability testing) and the regulators' needs for calibration and QA/QC materials. When the Clean Air Act Amendments (CAAA) of 1990 extended the CAAA to an additional 100 plus compounds, the repository no longer met the needs of the regulators. The CAAA also caused the EPA to change how it regulated stationary sources under the CAA. Historically, EPA had provided the regulated sources with EPA-validated or, at least well-characterized, pollutant measurement systems for monitoring the source's emissions. The CAAA's inclusion of many new toxic pollutants, combined with its emphasis on Maximum Achievable Control Technology (MACT), caused the EPA to adopt a performance-based approach to control stationary source emissions (somewhat analogous to the DRE approach used for incineration testing under the RCRA and the CERCLA). In this latter approach, the EPA provides regulated sources with general information on the test methods applicable to each regulated pollutant and requires the source to document that the test method used was accurate.

AREAL's inventory became inadequate because:

- 1) Most of the 50 newly-identified toxic and 60 oxidant precursor VOCs were not in the AREAL repository and/or their stability in compressed gases was unknown.
- 2) Many of the VOCs were available only at concentrations significantly higher than those found in the gas streams exiting from control devices and their stability at these lower concentrations was unknown or, at best, suspect for extended storage periods (e.g., 3 to 6 months). (Since the MACT regulation depends on accurate measurement of the pollutant concentration(s) before and after the control device, accurately certified, stable gas mixtures are needed at the lower pollutant concentrations.)
- 3) Most of the toxic organics in AREAL's repository were

available only as binary (VOC plus balance gas) rather than as multi-component mixtures. (Because the CAAA requires some sources to simultaneously measure many toxic VOCs, multi-component VOCs standards are needed.)

Thus, at a time when the test method development and validation effort required from the regulated community was increasing significantly, reliable, accurately-certified reference materials were not available for many of the VOCs. To address this situation the AREAL : is revising the guidance on Protocol Gases; has instituted the Research Gas Materials (RGM) program at the NIST to provide well-characterized reference materials for situations where the development of SRMs is not justified<sup>(1)</sup>; is continuously auditing the suppliers of Protocol Gases<sup>(2)</sup>; has accelerated its efforts to develop stable, accurately-certified gaseous reference materials; and is developing a gas transfer system (GTS) that the regulators and the regulated can use to prepare small quantities of their own accurately-certified reference materials.

Using the GTS, organizations can prepare at relatively low cost a myriad of gas mixtures using a small number of master gas mixtures (\$200-\$10,000 each), a diluent gas (\$50-\$250 each) and reusable, low volume compressed gas cylinders (\$300-\$450 each). The GTS should be particularly useful when conducting DRE testing and assessing control device performance testing. It should also be very useful for gas mixtures whose long-term stability is known only for concentrations 10 to 100 times higher than those needed for the measurement systems.

The goal of our program is to provide each EPA regulatory unit with the design and performance specifications for a fully-validated, turnkey system they can use to prepare pollutant standards that meet their needs. A detailed instruction manual that describes how to operate, clean and maintain the gas transfer system and also lists the pollutants for which it is applicable will accompany these specifications. As the AREAL's research program identifies additional pollutants for which the system is applicable, this information will be provided to the EPA regulatory unit(s) affected. The design specifications and instruction manual will also be provided free-of-charge to any non-regulatory organization that requests them.

The GTS and the experiments that the AREAL is conducting to characterize it, are described below.

#### GAS TRANSFER SYSTEM

Developed in cooperation with Scott Specialty Gases Inc., Plumsteadville, PA the GTS employs a stainless steel manifold (Figure 1) containing eight diaphragm packless valves (items V-1 through V-8 in Figure 1), one bellows valve (item V-9 in Figure

1), two pressure gauges (0-400 psi and 0-2300 psi) and fittings to attach five compressed gas cylinders.

All internal parts of the manifold have been treated with Scott's Acuclean and Aculife processes. The manifold is mounted on a 3.2 mm thick aluminum plate which is mounted on a wall at ManTech Environmental Technology's Commercial Park West facility in Research Triangle Park, NC. To maintain a constant temperature, the GTS manifold is wrapped with heat tape covered with insulation material. All tubing-to-tubing and tubing-to-valve connections are either orbitally welded or are of the VCR type.

The manifold can accommodate two master cylinders, a diluent cylinder and two receiver (audit) cylinders such as the 11 cm OD x 25.4 cm long aluminum cylinders we are now evaluating for use with this gas transfer system. These audit cylinders have been treated with Scott's Acuclean and Aculife processes and pressure tested to 3000 psi. Their nominal volume at one atmosphere is 1.5 L, which corresponds to 220 L at 2200 psi. They and the other compressed gas cylinders attach to the manifold using a CGA to VCR adapter.

#### EXPERIMENTS TO CHARACTERIZE THE GTS Analytical System

The GTS can be used for inorganic and organic gas mixtures. Presently, we are studying only organic mixtures. Two or three samples are taken from each gas mixture (replicates) and analyzed as discrete samples using a cryogenic concentrating system and a HP 5890 Series II/HP 5970 GC/MSD system. For the gas transfer efficiency studies, the GC/MSD system uses the master gas mixture as the reference standard. For most of the compounds in the gas mixtures being evaluated, the precision of the analytical system is between 5 and 10%.

#### Leak-check of GTS

The GTS was found to be leak-free when pressurized to 350 psig with helium and checked for leaks with a helium leak detector.

#### Procedure to Clean Audit Cylinders

An eight-cycle pressurization (to 30 psig with VOC-free nitrogen)/evacuation (to 50 mm Hg) procedure effectively removed even ppm levels of the VOC checked to date. We have not yet attempted to optimize the cleaning procedure for the cylinders.

#### Procedure to Clean Audit Cylinder Regulators

Attaching the Model 19 regulator to a pressurized audit cylinder and letting the gas flow through the regulator for 70 minutes effectively cleaned even regulators from audit cylinders that had contained ppm concentrations of VOCs.

### Check of GTS Manifold Cleanliness

After the GTS system was assembled, a VOC-free gas was passed through it and collected in two precleaned audit cylinders and in two Summa polished S.S. canisters. No VOCs were found when the cylinders and canisters were analyzed. Similar results were obtained after the GTS had been used to fill audit cylinders with ppb and ppm mixtures and then cleaned using the eight-cycle pressurization/evacuation procedure described above. We have not yet attempted to optimize the cleaning procedure for the manifold.

### Transfer Efficiency Tests

The gas mixtures being used contain VOCs at the concentrations needed to make gas mixtures that will meet present regulatory requirements. The efficiency of transfer is being evaluated as a function of GTS temperature, gas concentration, VOC, audit cylinder pressure, GTS flow rate settings, and GTS dilution ratio. Since the precision of the analytical system is between 5 and 10% for most of the compounds, the target goal for efficient recovery is 90 to 110% of the nominal concentration.

Three gas mixtures have been studied to date:

Mixture A. A gas mixture containing 14 aromatic and chlorinated hydrocarbons at 3 to 14 ppm was used to fill two audit cylinders to 800 psig. The mean percent recoveries for 11 of the 14 VOCs were 90 to 110%; all percent recoveries were between 85 and 115%.

Mixture B. Three volumes of a gas mixture containing 20 aromatic and halogenated hydrocarbons at 5-10 ppb was blended with one volume of another mixture containing 9 unique alkane compounds at 20 ppb and the resulting mixture was placed in two audit cylinders to 800 psig. The mean percent recoveries for 13 of the 29 VOCs were between 90 and 110%; for 20 of the 29 they were between 85 and 115%.

Mixture C. A cylinder containing 34 oxidant precursor VOCs at 45ppb was used to fill two audit cylinders to 1530 psig. The mean percent recoveries for 33 of the 34 VOCs were between 90 and 110%.

### Stability Studies

The effects of cylinder pressure, gas mixture humidity, VOC concentration and storage conditions will be evaluated for 120-day periods. The following procedure will be used initially. Two audit cylinders will be filled to 2000 psig using the GTS and the gas transfer efficiency will be assessed. The two audit cylinders will be reanalyzed versus the master gas mixtures at 30 days, 60 days, 90 days and 120 days. After the 30-day analysis the pressure in one of the cylinders will be reduced to 1000 psig; after the 60-day analysis it will be reduced to 500 psig. Thereafter it will be analyzed without reducing the pressure after the analysis. Each gas mixture will be studied for

stability in the audit cylinders at 1000, 200 and 10 ppb.

#### Audit Cylinder to Sampling System Transfer Efficiency

If the gas mixtures cannot be quantitatively delivered from the audit cylinders to the measurement systems under field condition, the value of the GTS approach for the regulatory community will be reduced. Available gas delivery systems will be evaluated as a function of flow rate, VOC concentration, gas stream humidity/temperature, and audit cylinder pressure to develop reliable delivery systems for each gas mixture. The candidate delivery systems will be validated under laboratory and field conditions.

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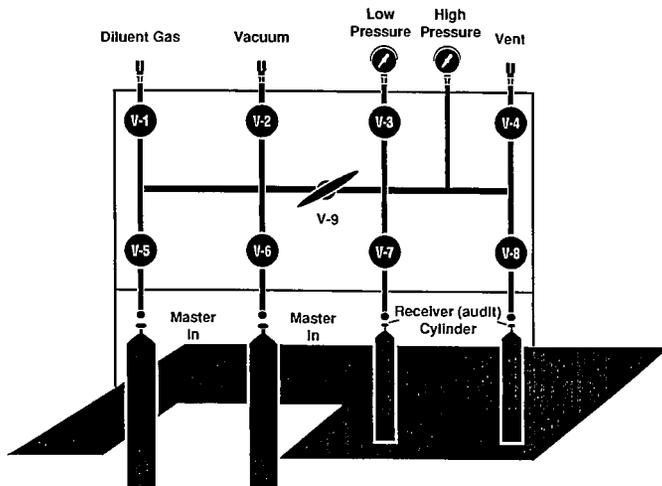
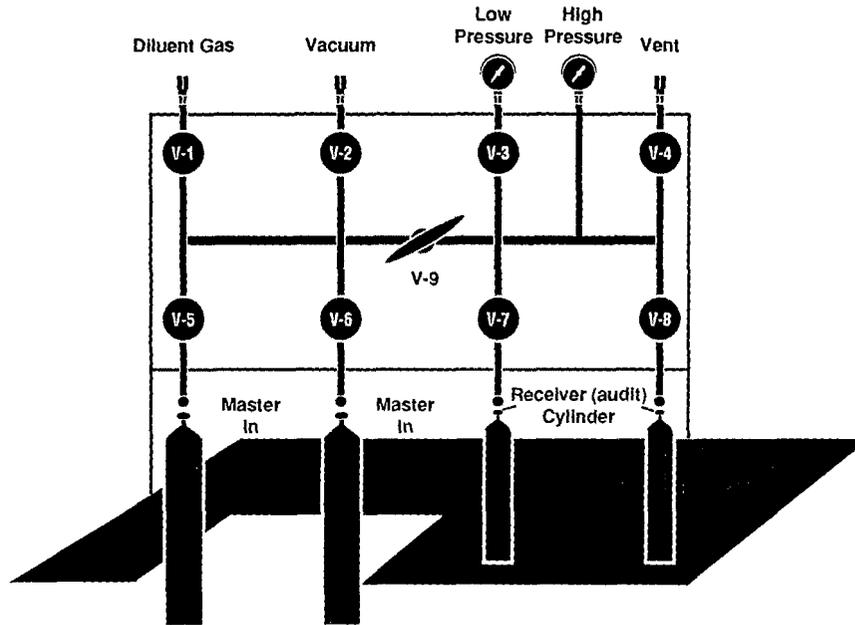


Figure 1. Gas transfill system

# Transfill System



## ROUND-ROBIN ANALYSIS OF PERFORMANCE EVALUATION SAMPLES BY STANDARD ARI 700-88

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### ABSTRACT

This paper describes the results of a round-robin interlaboratory study of analyses for selected contaminants in reclaimed refrigerant by Air-Conditioning and Refrigeration Institute (ARI) Standard 700-88. Performance evaluation audit samples for contaminant analysis of chlorofluorocarbon refrigerants were prepared using previously described techniques developed at the Research Triangle Institute (RTI). Four laboratories participated in the study. Four refrigerants were studied: R-11, R-12, R-22, and R-502. Three analytes -- impurity refrigerant, moisture, and high boiling residue (primarily compressor oil) -- were studied at two concentration levels. Level one was near the standard for reclaimed refrigerant and level two was at a higher concentration. For the impurity refrigerant analyses, the reported range of precision (relative standard deviation) was from 8 to 39%, with an average bias between -12.7 and +3.7%. For the moisture determination, precision ranged between 8 to 36% in the different CFC matrices, and bias ranged from -34.9 to +6.7. High boiling residue analyses yielded a precision range of 6 to 51%, and relative bias was between -18.7 and 59.5%. The major factors affecting total error appeared to be container effects such as cleanliness and wall adsorption; characteristics of the matrix refrigerants, including vapor pressure and affinity for water; and the variability among laboratories.

### INTRODUCTION

Chlorofluorocarbons (CFCs) have been employed in domestic and commercial refrigeration for over half a century. As a result of the spectacular success of this technology, a massive amount of these materials, which have been implicated in stratospheric ozone depletion and global climate change, is now in the installed base of refrigeration equipment. The existing stock of chlorine-containing refrigerants must be kept in use until replacement materials can be developed, manufactured, and phased into the marketplace. Meanwhile, recycling the refrigerants is an important means of minimizing disruption of the changeover while limiting further manufacture of CFCs. The Air-Conditioning and Refrigeration Institute (ARI) has published Standard 700-88 which provides recommended contaminant limits and methods of analysis to assess the quality of recycled refrigerants. The objective of the study reported here was to assess accuracy and precision of these techniques in an interlaboratory comparison study.

To determine levels of contaminants in refrigerants used in commercial refrigeration equipment, ARI conducted a field test in 1991. The purpose of this study was to determine the level of contamination that operating refrigeration equipment could tolerate before failure occurs. Ten different categories of refrigeration equipment were studied. Individual units were 3 to 6 years old. Procedures, methods, and target analyte levels similar to those of ARI Standard 700-88 were used for

this study. EPA provided Quality Assurance (QA) assistance to the ARI project by contracting with RTI to prepare several sets of performance evaluation audit (PEA) samples that contained selected contaminants of interest and to conduct an interlaboratory study of analytical performance. Clean refrigerants were spiked with known amounts of specified contaminants to make these samples. Sets of these samples were to be sent to the laboratory used in the ARI field study and to three other laboratories who routinely analyze contaminated refrigerants. RTI also analyzed one set and one set was kept in reserve. After the analyses were performed and the data sets reported, RTI conducted the statistical analysis and made a final report to EPA which attempted to characterize the components of variability in the data.

## DESIGN OF PROJECT

Four laboratories (RTI and three additional laboratories) participated in the round-robin analysis. The PEA samples consisted of refrigerants spiked with selected contaminants commonly found in recycled refrigerants. The contaminants chosen for the project consisted of impurity refrigerant, moisture, and high-boiling residue, which consists primarily of compressor oil and breakdown products. The CFC refrigerants chosen for study (R-11, R-12, R-22, and R-502) were the same refrigerants used in the ARI field study.

The PEA samples were prepared in RTI's laboratories using the methods described in "Preparation of Performance Evaluation Audit Samples for the Determination of Impurities in CFCs".<sup>1</sup> Each participating laboratory was sent a fully labeled set of audit samples in clean, high-pressure cylinders. Each set of audit cylinders was accompanied by a protocol for sampling and analysis which consisted of procedures supplied by the laboratory that analyzed the field samples for the ARI study, accompanied by notes describing RTI's experience in analyzing its set of audit samples using the ARI methods.

## ANALYTICAL METHODS

Impurity refrigerant was analyzed during the field study using a gas chromatograph/thermal conductivity detector (GC/TCD) with a packed column of porous polymer beads (Poropak). In the round-robin study, RTI used a gas chromatograph/flame ionization detector (GC/FID) with a packed column containing perfluoropolyether (5% Fluorocol) on a graphitized carbon black inert base (Carbopak B). Either method is allowable under the ARI Standard. The identity of the impurity refrigerant is determined by its retention time. A multipoint calibration curve was constructed for each refrigerant for accurate quantitation. Calibration standards were made by weight or volume (using the ideal gas law), depending on the laboratory. Concentrations of the impurity PEA samples were about 0.2% and 0.4%.

Moisture was determined as described in the method, ASTM E 700-79.<sup>2</sup> RTI performed the moisture analyses in a dry box to prevent uptake of water from the air. Methanol was changed after every sample. Blanks were determined using virgin refrigerant. Check standards consisted of organic liquid containing known levels of water.

High boiling residue by the Standard 700-88 method requires a volume of refrigerant to be evaporated and the volume of the remaining residue measured. In the prescribed method, a Goetz bulb is filled to the 100-mL mark with the refrigerant. After evaporation, the remaining residue flows into a high-precision calibrated sidearm. Because of the difficulty of filling the bulb with exactly 100 mL of the highly volatile refrigerant, the amounts of refrigerant and residue were also determined by weight.

## CALCULATIONS

### Partitioning Corrections

The participating laboratories conveyed the analysis results to RTI who evaluated and reported them to EPA. Because analyses are performed serially, internal evaporation in the pressurized cylinder causes the ratio of gas to liquid to shift, resulting in concentration changes. This problem is explained in detail in references 1 and 3. Accurate treatment of the data requires that the concentration of each analyte be corrected for the amount of refrigerant that has been removed from the container for prior analyses. For the data reported here, the magnitude of the correction ranged from negligible to about 6%, depending upon the refrigerant and the contaminant in question.

## RESULTS

### Impurity Refrigerants

Recoveries of the impurity refrigerants are shown in Table I. Recoveries ranged from approximately 50 to 150%, relative to the PEA preparation data. Individual laboratories tended to range either high or low, indicative of systematic intralaboratory bias. This interlaboratory variability was a significant contribution to the total error. The impurity analyses were not corrected for blanks because observed blank levels from virgin refrigerant were very small.

### Moisture

Moisture recoveries are shown in Table II. No systematic difference in average recovery could be seen between the two hydrophilic refrigerants (R-11 and R-12) and the two hydrophobic refrigerants (R-22 and R-502). Moisture blanks were too variable to justify correction of recoveries. Other factors affecting the moisture analysis may be container effects, difficulties inherent in the Karl Fischer technique, and properties of the refrigerant compounds.

Some of the problems associated with this analysis were (1) low levels: the moisture analyte was being measured in an atmosphere containing moisture amounts equal to or greater than the 15- to 200-ppm spike; (2) methanol depletion: the scrubber liquid tended to be depleted easily by the large volumes of gas passing through it which were necessary for obtaining adequate sample for analysis; (3) high blanks: there were occasional high blanks due either to incomplete cleaning of the sample cylinders or moisture with the refrigerant as it came from the manufacturer; and (4) lack of comparable check standards: standard materials for moisture in refrigerant have not been developed.

### High Boiling Residue

Residue recoveries by the volume method are shown in Table III, and ranged from about 50 to over 250%. Over half of the results were biased high, reflecting systematic bias with the analysis.

Two possible explanations for the observed bias are difficulties using the Goetz tube with the highly volatile refrigerants and container contamination.

Because of the high vapor pressure of three out of the four CFCs tested, a significant amount of material can boil away before the Goetz bulb can be filled to the prescribed 100- mL volume of refrigerant. To overcome this error, both the cylinder and Goetz bulb were weighed before and after the analysis. Results were obtained both from the volume analysis (as required by the Standard) and from the weight analysis. Residue recoveries by the weight method varied less, from about 80 to about 220% as shown in Table IV. This indicates that one source of bias may have been diminished, but other sources of error remain. An analysis based on weight measurements tended to lower the bias, but precision was still not good because of the small differences being calculated in comparison to the weight of the Goetz tube. Laboratory 3 developed a different protocol with a resulting recovery range of about 100 to 135%, much better than the other laboratories which followed the unmodified method.

Dirty sample containers may also have been a factor in the residue analysis. Some cylinders were not clean as evidenced by residual particulate matter in the blanks which sometimes equaled the low level (100-ppm) spikes.

## CONCLUSIONS

The primary measures of variability for this project were percent bias (bias%) and coefficient of variation (CV%) calculations. Bias% and CV% for all the analysis types are given in Table V.

Although the data from this study are limited, some trends emerged. The summary precision figures for the impurity analysis give an indication that the variation among laboratories was an important factor. This may be due to variability in methods of calibration standard preparation and to the use of different analysis methods (e.g., GC/TCD vs. GC/FID). The lack of precision in the moisture analyses may have been a result of instrumental and procedural difficulties. Precision and bias was uniformly high for the residue analyses except for the level 2 analyses by weight. Evidently the amount of spike residue at level 2 was great enough to overcome the errors introduced by use of unclean cylinders, and the errors involved with calculating small differences between large weights. The method of analysis by weight may be more accurate and precise than the current volumetric method.

Partitioning corrections were essentially insignificant to the calculation of impurity analysis recoveries, but could make as much as a 6% difference in the residue analysis, depending on the order of analysis. Impurity refrigerant was measured first, when the cylinder contents were nearly all in the liquid phase. Residue was measured last, when much of the refrigerant was in the gas phase, enriching the liquid phase in the residue.

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3. S.J. Wasson, Validation Study of Analytical Methods for Reclaimed Refrigerant, EPA report (in publication), U.S. Environmental Protection Agency, Research Triangle Park, NC, 1993.

Table I. Impurity refrigerant recoveries, percent (W/W).

Primary Refrigerant	Contaminant	Laboratory			
		1	2	3	4
R-11	R-12 level 1	99.2	113.3	94.9	ND*
	R-12 level 2	86.3	121.1	68.5	ND
R-12	R-22 level 1	74.2	101.9	80.1	125.5
	R-22 level 2	78.1	90.2	86.1	94.9
R-22	R-12 level 1	116.5	89.8	57.2	151.1
	R-12 level 2	97.2	95.7	57.2	102.8

Note: This table reflects no blank corrections.

\*ND = not determined

Table II. Moisture recoveries, percent (W/W).

Primary Refrigerant	Contaminants	Laboratory			
		1	2	3	4
R-11	H <sub>2</sub> O, level 1	90.7	116.8	49.1	125.9
	H <sub>2</sub> O, level 2	92.3	116.3	53.6	108.7
R-12	H <sub>2</sub> O, level 1	89.6	81.3	63.9	132.9
	H <sub>2</sub> O, level 2	65.8	52.1	52.6	90.0
R-22	H <sub>2</sub> O, level 1	91.4	87.6	101.1	105.7
	H <sub>2</sub> O, level 2	80.5	89.8	86.9	99.3
R-502	H <sub>2</sub> O, level 1	87.1	105.3	98.3	136.0
	H <sub>2</sub> O, level 2	65.5	93.3	88.5	73.6

Note: This table reflects no blank corrections.

Table III. Residue recoveries by volume method, percent (V/V).

Primary Refrigerant	Contaminant	Laboratory			
		1	2	3	4
R-11	Oil, level 1	159 ± 76	98 ± 42	72.9 ± .1	86.3
	Oil, level 2	52 ± 30	78 ± 25	120.2 ± .4	74.9
R-12	Oil, level 1	182 ± 40	210	140.4 ± .6	105.6
	Oil, level 2	85 ± 14	185	106.1 ± 18.2	71.3
R-22	Oil, level 1	68 ± 3	176 ± 65	175.8 ± 48.1	70.4
	Oil, level 2	141 ± 22	119	104.4 ± 14.8	92.0
R-502	Oil, level 1	113 ± 20	---	142.5 ± 5.0	143.9
	Oil, level 2	169 ± 19	261	128.9 ± 21.2	70.7

Table IV. Residue recoveries by weight method, percent (W/W).

Primary Refrigerant	Contaminant	Laboratory			
		1	2	3	4
R-11	Oil, level 1	173 ± 50	121 ± 53	135 ± 8	80.5
	Oil, level 2	130 ± 14	98 ± 7	124 ± 5	108.5
R-12	Oil, level 1	218 ± 28	150	120 ± 2	80.0
	Oil, level 2	128 ± 28	125	106 ± 4	92.6
R-22	Oil, level 1	156 ± 27	133 ± 18	132 ± 8	118.2
	Oil, level 2	111 ± 11	116	101 ± .4	101.5
R-502	Oil, level 1	129 ± 47	133	128 ± 2	295.2
	Oil, level 2	104 ± 15	115	104 ± 3	80.9

Table V. Data quality indicators.

Contaminant		Precision (CV%) <sup>1</sup>				Bias (%) <sup>2</sup>			
		R-11	R-12	R-22	R-502	R-11	R-12	R-22	R-502
Impurity,	level 1	9.4	24.4	38.5	---	2.5	-4.6	3.7	---
	level 2	29.1	8.2	23.7	---	-8.0	-12.7	-11.8	---
Moisture,	level 1	36.0	31.9	8.7	19.6	-4.4	-8.1	-3.5	6.7
	level 2	30.1	27.3	8.8	16.1	-7.3	-34.9	-10.9	-19.8
Residue, (volume)	level 1	36.5	28.8	50.3	13.1	4.1	59.5	22.6	33.1
	level 2	35.0	45.4	18.5	50.8	-18.7	11.9	14.1	57.4
Residue, (weight)	level 1	30.0	41.0	11.6	48.2	27.4	42.0	34.8	71.3
	level 2	12.7	14.8	6.8	14.2	15.1	12.9	7.4	1.0

CV% = (standard deviation/mean)100

Bias% = recovery % - 100%

EPA'S QA Program on the Suppliers of  
Protocol Gases

by

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**ABSTRACT**

In 1992, EPA's Atmospheric Research and Exposure Assessment Laboratory initiated a nationwide QA program on the suppliers of EPA Protocol Gases. The program has three goals: to increase the acceptance and use of Protocol Gases by the air monitoring community, to provide a QA check for the suppliers of these gases, and to help the users of these gases identify suppliers who can consistently provide accurately certified Protocol Gases. In this QA program which operates continuously, Protocol Gases are procured by EPA and the supplier's certification of the pollutant concentration(s) is verified by EPA. The results are published on the EPA Technology Transfer Network's electronic bulletin board. If a supplier's concentration differs from EPA's by more than 2%, the supplier is notified in writing immediately. The results obtained for SO<sub>2</sub>, CO and NO Protocol Gases are presented.

## INTRODUCTION

The Atmospheric Research and Exposure Assessment Laboratory (AREAL) of the U.S. Environmental Protection Agency (EPA) has begun a nationwide audit of the vendors of Protocol 1 (stationary source) and Protocol 2 (ambient air) Gas Standards. The intent of this program is as follows:

- Increase the acceptance and use of Protocol Gases as secondary standards by the air monitoring community.
- Provide a quality assurance check for the vendors of these gases.
- Assist users of Protocol Gases to identify vendors who can consistently provide accurately certified Protocol Gases.

## PROCEDURE

Either directly or through third parties, EPA continually procures Protocol Gases from commercial sources, checks the accuracy of the vendors' certification of concentration, and examines the accompanying documentation for completeness and accuracy.

For Protocol Gases the maximum allowable deviation from the certified value is 2%. Accuracy of the certification is checked using Standard Reference Materials (SRMs). If the difference between the EPA-determined and the vendor-determined concentration is more than 2%, or if the accompanying documentation is incomplete, EPA notifies the vendor immediately to resolve and correct the problem.

Results of EPA certification checks are placed on two bulletin boards, EMTIC (Emission Measurement Technical Information Center) and AMTIC (Ambient Monitoring Technology Information Center), on the Technology Transfer Network of the EPA Office of Air Quality Planning and Standards. Also included are notes describing any corrective action taken by a vendor after being notified of a problem with a Protocol Gas.

Bulletin board entries are organized in tables by gas (all nitric oxide results, for instance, are summarized in one table) and by vendor. Numerical data are supplemented by narrative footnotes explaining the results of any corrective action taken by the vendor. Thus the entries provide a continuous record of all audit activities. Table 1 lists the information presented on the bulletin boards. The bulletin boards can be accessed by following the procedure in Table 2.

Users who believe that their Protocol Gas has been certified incorrectly may contact Ms. Avis Hines of EPA/AREAL (919-541-4001) to request an EPA certification check. If EPA

accepts the gas cylinder for testing, the results of these tests will also be posted on the bulletin boards.

#### REQUIRED DOCUMENTATION

The Protocol Gas procedure requires two types of documentation to accompany the gas cylinder: a Certificate of Analysis, which may be mailed separately or attached to the cylinder; and a cylinder tag which must be attached to the valve under the valve cap. Documentation is incomplete until the vendor provides every item required to be on the certificate and on the tag.

#### RESULTS

This section of the audit report, organized by gas and by vendor, is updated whenever EPA conducts a new audit or receives corrective action reports from a vendor. It allows users of Protocol Gases to easily review the comparative performances of the vendors.

The standard of comparison used throughout the subsequent tables is the relative percent difference between the vendor and the EPA values with the EPA-determined concentration serving as the reference value.

Tables summarize audit results for each gas, with footnotes describing corrective actions taken by the vendors. Each vendor is assigned a footnote letter; all notes pertaining to that vendor will be listed chronologically in one place. If a vendor has more than one plant, each plant is assigned its own footnote. Notes may not be necessary for every vendor on every audit.

For the first three audits (nitric oxide, sulfur dioxide and carbon monoxide), gas cylinders obtained through third parties were analyzed in triplicate by EPA and by another laboratory. Each laboratory used its own SRMs, followed the Protocol Gas certification procedure, and reported the analytical results using both the linear regression method and the ratio method specified in the procedure. Because a statistical analysis showed that the results from EPA and the independent laboratory were indistinguishable, only the EPA results are now shown on the bulletin boards. The other independent laboratory serves as a referee laboratory whenever differences occur between results from EPA and the vendors.

#### Nitric Oxide

The eight vendors passed the analytical part of the audit for nominally 40 ppm nitric oxide. Five vendors provided incomplete documentation; upon notification of the deficiencies, the vendors immediately provided the missing items.

## Sulfur Dioxide

Only three of the eight vendors had cylinders of nominally 50 ppm sulfur dioxide which passed the analytical part of the audit. Incomplete documentation continued to be a problem. Only one vendor had both an acceptable value and complete documentation.

A review of vendor documentation revealed that cylinders from three vendors were certified by the same laboratory. All three, failing the EPA analyses and suspecting a problem with the standard used, recalled their cylinders for re-analysis.

## Carbon Monoxide

The eight vendors passed the analytical part of the audit for the nominally 40 ppm carbon monoxide. Incomplete documentation, however, remained a problem five of the eight vendors did not provide complete documentation until EPA contacted them.

## Disclaimer

The information in this document has been funded wholly by the United States Environmental Protection Agency. It has been subjected to Agency review and approved for publication.

Table 1. Information presented on the electronic bulletin boards

1. Vender name and location
2. Cost of Protocol Gas
3. Vendor gas concentration/date of analysis
4. EPA gas concentration/date of analysis
5. % difference from EPA concentration (Max 2%)
6. Accuracy and completeness of documentation
7. Corrective action taken by vendor

Table 2. Procedure for accessing the OAQPS TTN electronic bulletin boards

Note: One must be a registered user of the TTN to access the EMTIC or the AMTIC. For information on how to become a user call 919-541-5384.

The procedure to download and subsequently print the Protocol Gas audit document depends on the communication software used to connect to the TTN and the software used to work with text files. However, if you just want to view the document on the screen follow the steps below:

**EMTIC:**

1. Connect to the OAQPS TTN.
2. Enter your last name, first name, and password when prompted.
3. From the Top Menu of OAQPS TTN choose <B> EMTIC.
4. When prompted, choose <C> continue on to EMTIC.
5. From the EMTIC BBS Menu choose <D> EMTIC Documents.
6. From the next Menu choose <T> ORD/AREAL Documents
7. A list of files will appear which will include the audit document called "PROTOGAS.TXT"
8. To view the document type "*p l protogas.txt*".
9. For instructions on how to download the document using your particular communication program refer to the OAQPS TTN User's Manual or call their Help line (919-541-5384)

**AMTIC:**

1. Same as steps 1 and 2 above.
2. From the Top Menu of OAQPS TTN choose <I> AMTIC.
3. From the AMTIC BBS Menu choose <O> Available Related Documents.
4. From the next Menu choose <T> ORD/AREAL Documents
5. A list of files will appear which will include the audit document called "PROTOGAS.TXT".
6. To view the document type "*p l protogas.txt*".
7. For instructions on how to download the document using your particular communication program refer to the OAQPS TTN User's Manual or call their Help line (919-541-5384).

## ONE SIZE DOES NOT FIT ALL: A PANEL DISCUSSION ON QA APPROACHES TO AIR TOXIC ISSUES

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A panel of Quality Assurance managers from various EPA research laboratories and program offices in the Research Triangle Park convened to discuss quality assurance approaches to air toxic issues at Session 9 of the 1993 AWMA/EPA International Symposium. The panelists included Ronald K. Patterson (AREAL), Judith S. Ford (AEERL), Ronald R. Rogers (HERL), Rick Johnson (OIRM), and Gary Johnson (QAMS).

During the introduction, the importance of applying quality assurance/quality control (QA/QC) to data collection activities was stressed. It was also emphasized, however, that because of the large diversity in the research activities and objectives of the laboratories and program offices, the nature of the QA/QC activities varied considerably within each organization.

After the panel members were introduced, each made a presentation on the mission of their organization, how QA was currently being used in the organization, and the types of QA needed. Following is a summary of each presentation.

### **Ronald K. Patterson**, QA Manager for the Atmospheric Research and Exposure Assessment Laboratory

Mr. Ron Patterson began by giving a description of his organization. The Atmospheric Research and Exposure Assessment Laboratory (AREAL) operates under the EPA Office of Research and Development. The Laboratory employs 222 scientists and technicians, mostly in the disciplines of chemistry, physics, meteorology, and computer science. The basic mission of AREAL is to conduct intramural and extramural research related to air pollution exposure assessment and the collection and characterization of air pollutants emitted from stationary, mobile, and biogenic sources. This mission includes the study of air pollutant formation, transformation, and transport mechanisms; the study of source-receptor relationships; the assessment of human and ecosystem exposures to air pollutants; the development and application of predictive mathematical models; the development of instrumental and analytical methods; and the study of air pollution trends and patterns. AREAL also provides support and technical assistance to the regulatory and enforcement sides of the Agency and to state and local governments.

Mr. Patterson explained that to achieve the support aspects of this mission, AREAL published air pollution QA/QC guidelines in the Code of Federal Regulations (CFR Part 58) and developed the five-volume "Quality Assurance Handbook for Air Pollution Measurements" (the "Red Books"). The Laboratory also prepares standards, conducts audits on criteria air pollutants, and conducts research and development on non-criteria pollutant standards, audit devices, and Certified Reference Materials (CRMs). These activities are the responsibility of AREAL's Quality Assurance and Technical Support Division.

Mr. Patterson emphasized that the diversity of such a laboratory demands a flexible QA program. Since the bulk of the activities in the Laboratory are of a research and development nature, the QA program must focus on more than data collection. AREAL is beginning to focus on the "quality of science," value-added quality systems, and up-front planning with clear objectives, well-documented implementation plans, timely project assessment, corrective action, and peer review of the final product. These are essential quality systems for AREAL. The Laboratory also emphasizes the customer/supplier relationships associated with projects and maintains a strong customer focus. The quality systems approach attempts to foster teamwork and sharing between the customer and supplier and strives to manage the quality of project outputs. In conclusion, AREAL has determined that there is no "cookie-cutter" approach and is very aware that "one size does not fit all."

**Judith S. Ford**, QA Manager for the Air and Energy Engineering Research Laboratory

The Air and Energy Engineering Research Laboratory (AEERL) develops and assesses methods and technologies for preventing or reducing the deleterious effects of air pollutants on human health and welfare, and on the global environment. Applied research is conducted by the Global Emissions and Control Division (GECD) and the Pollution Control Division (PCD).

Ms. Judy Ford explained that the GECD is primarily concerned with atmospheric environmental problems. Such problems include global climate change, stratospheric ozone depletion, ozone nonattainment, air toxics, alternative fuels, accidental releases, and acid deposition. The other division, PCD, is concerned with air pollution associated with nitrogen oxides and combustion-related air toxic pollutants; fine particles and toxic particulate matter; hazardous, municipal, and medical waste incineration; radon in new and existing buildings; and indoor air pollutants.

Ms. Ford stated that direct support to measurement activities directed or performed by these two divisions is provided by AEERL's QA program. The program is guided by an Agency-approved QA Program Plan, which delineates QA requirements of Laboratory measurement activities. Examples of requirements are each data-gathering project must be planned for and approved prior to initiation of tests; long-term demonstrations and projects with a direct

impact on standard-setting or major decision making must be audited; and the data quality of results must be documented in EPA publications. Ms. Ford also informed Session attendants that several of AEERL's innovative QA tools have been adopted by other groups in the Agency, the two most notably being the QA four-category approach and the QA tracking system.

In summary, Ms. Ford stated that AEERL's QA program is a structured system not typical of many research laboratories. This is due primarily to the multidisciplinary nature of the Laboratory's research programs and its need for expertise in measurement-related fields, such as the chemical and statistical sciences.

### **Ronald R. Rogers**, QA Manager of the Health Effects Research Laboratory

Mr. Ron Rogers began by stating the Health Effects Research Laboratory's (HERL's) mission: to perform credible, high quality research that will improve EPA's ability to assess environmental health risks, and to provide advice on the interpretation and integration of scientific data for risk assessment and regulatory decisions. He continued by explaining that HERL is the focal point for toxicological, clinical, and epidemiological research within the Agency. The research program develops and applies state-of-the science biological assays, predictive models, and extrapolation methods which serve as the basis for the Agency's health risk assessments.

To fulfill its objectives, EPA must be both a regulatory and a science agency. Mr. Rogers described the risk assessment process which the Agency uses to establish and enforce regulations. This process includes four primary elements:

- **Hazard Identification:** Is the agent capable of causing an adverse effect?
- **Dose-Response Assessment:** What is the quantitative relationship between dose and effects?
- **Exposure Assessment:** What exposures occur or are anticipated?
- **Risk Characterization or Estimation:** Based on the results of dose-response and exposure assessments, what is the estimated health risk at anticipated exposures?

Of the first three, which are the primary data-generating elements, the Agency has historically focused on data quality issues related to exposure assessment for a variety of scientific, socio-political, and economic reasons. HERL research, however, is primarily focused on the areas of hazard identification and dose-response, with some effort applied to exposure assessment. Logically, says Mr. Rogers, the quality of the

hazard identification and dose-response data on which regulatory standards are set is paramount to the effective and efficient protection of human and ecological health. Unfortunately, because biological responses and standards against which one can compare these biological responses are virtually nonexistent, traditional ideas about evaluating and controlling the quality of such data are often not useful. Mr. Rogers explained that HERL does utilize laboratory-wide QC activities that are focused on instrument maintenance and calibration to help ensure the quality of certain types of measurement data, but must rely on other approaches to confirm the quality of graded response, dichotomous response, or other types of health effects data. HERL has chosen to ally available traditional QA activities with an expanded emphasis on review by peers. HERL also has a strong biostatistics staff to support investigators in the development of appropriate experimental designs. A prospective, in-progress, and retrospective peer review program would enable HERL to build quality management into strategic research planning while also taking better advantage of scientific expertise to judge the quality of HERL research and the data it produces. Mr. Rogers also said that HERL is currently working to create a system whereby alliance of peer review with QA can be as practical as it is logical.

**Rick Johnson**, Office of Information Resources Management

Mr. Rick Johnson began by describing EPA's development of Good Automated Laboratory Practices (GALPs). Corruption of computerized data by its contractors and a follow-up national survey of laboratory data management practices prompted EPA's Office of Information Resources Management (OIRM) to develop GALPs. GALPs are recommendations to EPA's national programs of procedures and practices to follow in developing data for EPA's use in regulating the environment in laboratories that employ automated data collection, processing, storage, and retrieval technologies.

Mr. Johnson said that the escalating popularity of the GALPs is a case study that public and private sector regulatory managers should examine. A conflicting argument can be made that the need for GALP-like specifications is largely the reason for this atypical enthusiasm for regulatory guidance. According to Mr. Johnson, however, an equally compelling statement can be made that the GALPs simply make good sense for federally regulated industries, for suppliers of laboratory automation technology, and for national and international regulatory organizations and associations to adopt.

Mr. Johnson explained that the GALPs are a union of two fundamental sets of established principles: the Agency's Good Laboratory Practices (GLPs) and its Information Resource Management Policies (IRMs). The GLPs specify a minimum set of basically manual procedures for manufacturers of pesticide and chemical products to follow when submitting health and safety data to the Agency. The GLPs were also developed after EPA found that laboratory data used by the Agency to regulate pesticides were unreliable. The Agency's IRM Policies prescribe procedures and

practices that must be followed when using automated data processing (ADP) technology. These IRM standards have been widely used for almost two decades.

Management of EPA's information resources is OIRM's primary responsibility that it executes through the development of ADP policies and oversight of ADP-related acquisitions.

**Gary L. Johnson**, Quality Assurance Management Staff

Mr. Gary Johnson concluded the panel presentations. His organization, the Quality Assurance Management Staff (QAMS), is directed by EPA Order 5360.1 to establish policies and procedures for planning, implementing, and assessing the effectiveness of quality systems in support of environmental programs. Such quality systems include traditional QA/QC activities, as well as the necessary management systems elements for conducting the quality management process. QAMS is also responsible for developing the requirements and guidance documents needed to plan, implement, and assess the individual quality systems established by EPA program offices, Regions, and research laboratories. Moreover, QAMS is responsible to senior Agency management for the oversight and periodic assessment of these quality systems to ensure their effectiveness and sufficiency.

Mr. Johnson explained that during the past decade, the objectives and missions of many EPA organizations have changed in order to satisfy evolving environmental issues and concerns. Similarly, the EPA quality system requirements have changed to reflect this evolution. He emphasized that the keystone of all environmental programs is that environmental data must be of the type and quality needed and expected to support decision affecting rulemaking, enforcement actions, research, and other needs.

According to Mr. Johnson, this year EPA anticipates the adoption of a new national consensus standard as the basis for its internal quality system: "Quality Systems Requirements for Environmental Programs" (ANSI/ASQC E4-1993). This standard will be the first American National Standard for environmental quality systems when it is published. EPA has begun the development of new and revised requirements and guidance documents to implement this standard within the Agency. Mr. Johnson said that later, changes will be sought in the acquisition and financial assistance regulations to require those organizations who receive contract funds or financial assistance funds to also comply with this standard. These documents will begin to be available after this summer and through the next 12 to 18 months. The documents will become part of an Agency internal Quality Manual, along with a revised EPA Order on quality management, that will undergo Agency-wide consensus review and approval later this summer.

In a parallel effort this summer, Mr. Johnson announced that QAMS will implement an extensive management assessment of environmental data operations across EPA using the Management Systems Review (MSR) process. The MSRs will examine the quality systems applied to key environmental programs to determine their effectiveness and provide feedback to management on opportunities for improvement. Air toxics and related programs will be among those programs reviewed in the next few years, along with other critical Agency regulatory and research programs.

Mr. Johnson concluded that change is inevitable and the upcoming changes in the EPA quality system will provide consistency and sufficiency for the remainder of the 1990s and beyond.

*Session 10*

*Source Emissions*

*and Measurements*

# DEVELOPMENT OF A TEST METHOD FOR THE MEASUREMENT OF GASEOUS METHANOL EMISSIONS FROM STATIONARY SOURCES

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## ABSTRACT

Methanol was designated under Title III of the Clean Air Act Amendments of 1990 as a pollutant to be regulated<sup>1</sup>. The U.S. EPA, through a contract with Research Triangle Institute, has developed a test method for the measurement of methanol emissions from stationary sources. The methanol sampling train (MST) consists of a glass-lined heated probe, two knockout traps and three sorbent cartridges packed with Anasorb<sup>®</sup>747, a beaded, activated carbon. Anasorb<sup>®</sup>747 samples are desorbed with a 1:1 mixture of carbon disulfide and N,N-dimethylformamide. Samples are analyzed by gas chromatography with flame ionization detection.

Following laboratory testing, field tests of the MST and the National Council for Air and Stream Improvement (NCASI) sampling method for methanol were conducted at a paper and pulp mill. The sampling location was an inlet vent to a softwood bleach plant scrubber. In accordance with EPA Method 301<sup>2</sup>, two pairs of trains were run in parallel for six runs, collecting a total of twenty-four samples by each method. During each test run, half of the trains were spiked with a known amount of methanol. The average percent recovery of the spike was higher for the MST method than for the NCASI method. Both methods had a relative standard deviation of less than 5 percent. The practical quantitation limit (PQL) was about 2 ppm for the MST method.

## INTRODUCTION

A literature search was conducted to review the chemistry of methanol and the sampling and analysis methods that are currently used to measure methanol. The methanol sampling train (MST) was developed from information obtained from the literature search and was evaluated in the laboratory. The MST (Figure 1) consists of a glass-lined heated probe, two knockout traps in an ice bath, and three sorbent cartridges packed with Anasorb<sup>®</sup>747 (SKC). The Anasorb<sup>®</sup>747 (or equivalent) is used to collect methanol and has a recovery efficiency of 98.1 percent. The knockout traps, used to remove water vapor, also collect a significant amount of methanol. A 1:1 mixture of carbon disulfide and N,N-dimethylformamide is used to desorb the Anasorb<sup>®</sup>747 samples. Condensate and desorption samples are analyzed by gas chromatography with flame ionization detection. The MST allowed recovery of about 98 percent of methanol sampled during the laboratory evaluation.

A field evaluation of the MST and the National Council of the Paper Industry for Air and Stream Improvement (NCASI) sampling method for methanol (Figure 2) was conducted at a pulp and paper mill. The sampling location was an inlet vent to a softwood bleach plant scrubber. Four trains were run in parallel (as two pairs) for six runs, collecting a total of twenty-four samples by

each method. Half of the trains were spiked with a known amount of methanol during each test run. The average percent recovery of the spike was 108.3 percent for the MST method and 81.6 percent for the NCASI method. Although neither method showed a significant bias at the 95 percent confidence level, the biases of the two methods were significantly different. The practical quantitation limit (PQL), as defined in Section 9 of EPA Method 301, was about 2 ppm for the MST method.

## Laboratory Evaluation

**Sorbent Tests.** The Occupational Safety and Health Administration (OSHA) recently promulgated a method for methanol (OSHA Method 91) which used Anasorb<sup>®</sup>747 as the collection medium. A literature review indicated that Anasorb<sup>®</sup>747 was the most promising sorbent for the collection of methanol.

The desorption efficiency of methanol from Anasorb<sup>®</sup>747 was determined at three different loadings. A primary methanol standard (94.8 µg/mL) was prepared by diluting 3 mL of methanol to 25 mL with deionized water. Five grams of Anasorb<sup>®</sup>747 was placed in each of three separate vials, which were then spiked separately with 3 µL, 6 µL, and 9 µL of the methanol standard. The Anasorb<sup>®</sup>747 in each vial was desorbed with 30 mL of a 1:1 mixture of CS<sub>2</sub> and DMF. The average overall recovery for multiple runs of the three samples was 98.1 percent, indicating that methanol could successfully be recovered from Anasorb<sup>®</sup>747.

**Sampling Apparatus.** A dynamic dilution system was used for mixing methanol and diluent humidified nitrogen. The components were mixed in a 1-liter dilution flask. The flowrates of the test gas and the humidified nitrogen were regulated with Tylan<sup>®</sup> mass flow controllers. The gas mixture was passed from the dilution flask to a three-port manifold. The dilution flask and manifold were enclosed in an insulated, temperature-regulated box. A cylinder containing 250 ppm methanol was used as the test gas and was diluted to the desired concentration using the system described above.

The sampling train consisted of two condensate traps in an ice bath, three Anasorb<sup>®</sup>747 sorbent cartridges and a pump. The sorbent cartridges were modified VOST tubes where the back end was replaced with a #7 Ace-Thred<sup>®</sup> joint. A Nutech<sup>®</sup> VOST control module was used as the pump. The sampling parameters were 1.0 L/min for twenty minutes.

**Breakthrough of a Methanol Spike.** The capacity of the MST was tested by conducting three runs where 4 mg of methanol was spiked onto the train. All runs were conducted at 1 L/min. For runs 1 and 2, the front tube contained 3 g Anasorb<sup>®</sup>747 and the middle and back tubes contained 1.5 g Anasorb<sup>®</sup>747. Thirty liters of gas was sampled for the first run. No methanol was found on the back tube and less than 5 percent was found on the middle tube. When the sample volume was increased to 60 L for run 2, more than 4 percent of the methanol was found on the back tube and nearly 20 percent was found on the middle tube, indicating significant breakthrough. For the third run, 5 g of Anasorb<sup>®</sup>747 was placed in the front tube and 60 L of gas was sampled. No methanol was found on the back tube and less than 4 percent was found on the middle tube. The third run showed that the MST could collect a significant amount of methanol without breakthrough. The average recovery of the spike for the three runs was 97.6 percent.

**Analytical Systems and Performance.** The methanol samples were analyzed on a 30-m DB-Wax megabore column with a flame ionization detector. The temperature program started at

50°C, then increased 10°C/min to a final temperature of 140°C. A conversation with NCASI personnel indicated there were five possible interferants: chloroform, acetone, acrolein, methyl ethyl ketone (MEK), and dichloromethane. Methanol was separated from these interferants by the employment of a 60-m column. The analytical limit of quantitation was 0.7 ng for the Anasorb<sup>®</sup>747 samples and 0.5 ng for the condensate samples.

Sample Stability. The stability of methanol on Anasorb<sup>®</sup>747 was tested by spiking twelve Anasorb<sup>®</sup>747 tubes. Three tubes and a blank were analyzed on the day of the spike (day 0), and on days 3, 7, and 14. The recovery of methanol from Anasorb<sup>®</sup>747 on days 0, 3, 7, and 14 was 102, 80, 86, and 89 percent, respectively.

### **Field Testing and Method Validation**

Field testing of the MST was conducted at two different sites. The primary objective of the field testing was to validate the MST in accordance with EPA Method 301 procedures. A secondary objective was to compare the MST to the NCASI method for sampling methanol. Each field test consisted of four MSTs run in parallel for six runs (24 samples total). The four trains were run as two pairs, with the two probes of each pair taped together and placed perpendicular to the vent (or stack) and to the other pair. The method validation procedure used for the MST was also used for the NCASI method.

Field Site A: Thermomechanical Pulping Mill. The first field site was the stack from an atmospheric cyclone at a thermomechanical pulping (TMP) mill. Analysis of the samples from the first pre-survey indicated that no methanol was collected. After consultation with various plant personnel, it was learned that the process had two modes: the steam could pass through the cyclone or it could bypass the cyclone and be forced out the stack. The pre-survey samples had apparently been collected while the steam was passing through the cyclone, which removed water and methanol.

During a second pre-survey at the TMP site, an attempt was made to collect samples while the steam was being forced through the vent, bypassing the cyclone. The first run was stopped after 30 seconds because condensed steam had filled the condensate knockout traps. The temperature of the stack gas was measured at 212°F, indicating that the gas was nearly all water. Because sampling conditions were unsuitable for both methods, selection of a second field site was necessary.

Field Site B: Softwood Bleach Plant. The second field site was a 3-foot diameter inlet vent to a softwood bleach plant scrubber at a pulp and paper mill. The vent gas temperature was just above 130°F.

On the first day of sampling, seven NCASI runs were performed. A seventh run was necessary because the first run was performed at a flow rate of 0.5 L/min rather than 1.0 L/min. Each run lasted 30 minutes and a sample volume of 30 liters was collected. Each pair of trains was alternately spiked with 6 µL of a methanol standard. The methanol standard was prepared by diluting 3 mL methanol to 25 mL with deionized water, resulting in a concentration of 94.8 µg/mL. Thus, each spike contained about 569 µg methanol, approximately the same amount as collected during each run.

The MST method was tested on the second day of sampling. Each MST was to have three sorbent tubes, packed with 5 g, 1.5 g and 1.5 g of Anasorb<sup>®</sup>747. However, one of the nylon bushings required to connect the sorbent tubes was missing. This resulted in the second train of pair 2 having only two tubes, containing 5 g and 1.5 g of Anasorb<sup>®</sup>747, for all runs. As a precautionary measure, a seventh run was conducted to ensure enough valid samples for a meaningful statistical

analysis. Each pair was alternately spiked with 6  $\mu\text{L}$  of the methanol standard. The heated probes were inserted about eighteen inches into the 3-foot. vent.

The paired trains for each method showed good precision with a standard deviation below 4 percent. The average spike recovery for the MST (Table 1) was considerably higher than for the NCASI method (Table 2): 108.3 percent compared to 81.6 percent. The methods had nearly identical average unspiked concentrations, but the average measured concentration of spiked samples from the MST was higher than the average measured concentration of spiked samples from the NCASI sampling trains. The reason for this difference is unknown. Both methods had a similar, and rather high, standard deviation of their spike recoveries. The high standard deviation of the spike recoveries was due to a bias that existed between the two pairs of trains. Pair 2 gave results that were consistently about 6 percent higher than the results from pair 1. As a result, when pair 2 was spiked, there was a high spike recovery, and when pair 1 was spiked, there was a low spike recovery. The spike recovery for pair 2 averaged about 27 percent higher than the spike recovery for pair 1. This discrepancy was found for both methods and the cause is unknown. Because of the precision between the trains of each pair, it is unlikely that there was a leak problem.

## CONCLUSIONS AND RECOMMENDATIONS

The MST and NCASI methods both met the guidelines specified by EPA Method 301. Both methods showed good precision and their precisions were not significantly different at the 95 percent confidence level. Even though the bias of the NCASI and MST methods were not significant, there was a significant difference in bias at the 95 percent confidence level. While the reason for this difference is unknown, it is possible that the heated glass-lined probes and heated injection ports used to spike the MSTs were more efficient at transporting methanol than the unheated teflon sampling lines and injection ports used to spike the NCASI sampling trains.

An advantage of the MST is that the composition of the emission source can be determined by using a mass spectrometric detector to analyze the Anasorb<sup>®</sup>747 samples. Emissions at the field site used in this study contained no compounds at detectable concentrations other than methanol. A field test at a site with a more complex emission matrix would provide important information about the capabilities of the MST method. A field test at a site with a higher methanol concentration could help determine the collection capacity of the MST and if there could be problems with breakthrough. Although the MST has collected large amounts (5 mg) of methanol in the laboratory without breakthrough, it is unknown what effect other chemical species in the stack gas may have on this capacity. The MST also needs to be modified so that it can sample high temperature gas streams with high water content without flooding the train components.

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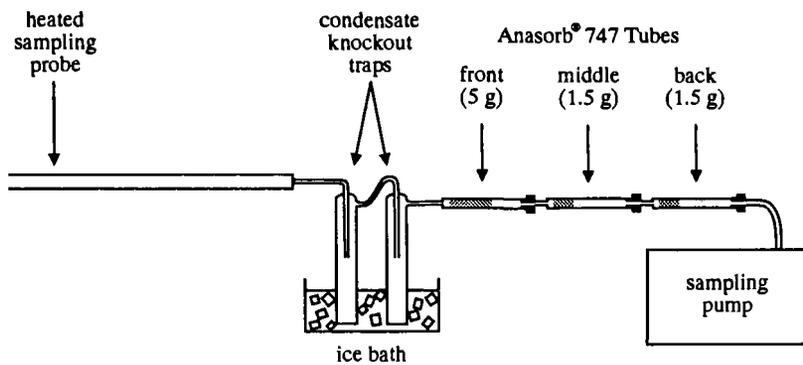


Figure 1. Methanol sampling train.

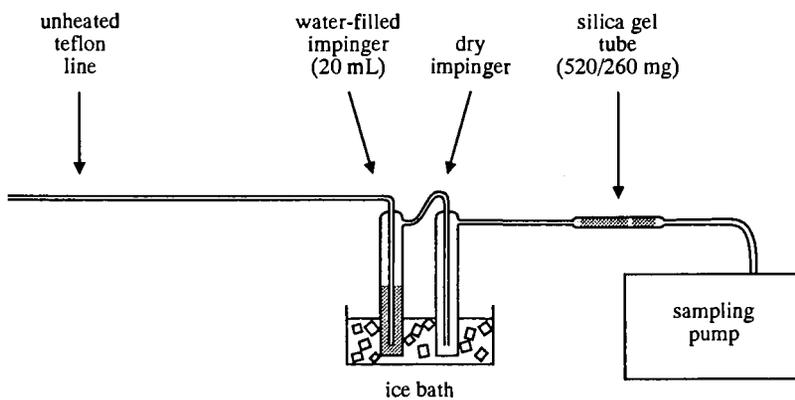


Figure 2. NCASI sampling train for methanol.

**Table 1. Percent recoveries of field test spikes for the MST method.**

	Average Concentration of Sample With Spike (ppm)	Average Concentration of Sample Without Spike (ppm)	Average Measured Spike (ppm)	Average Spike (ppm)	Percent Spike Recovery
8	42.98	31.27	11.72	13.32	87.9
9	44.99	25.23	19.77	13.85	142.7
10	43.88	29.03	14.86	13.21	112.5
11	47.94	32.42	15.52	13.90	111.6
12	46.13	34.03	12.10	13.02	93.0
14	44.18	30.55	13.63	13.33	102.2
Mean	45.02	30.42	14.60	13.44	108.3
Std. deviation	1.79	3.06	2.94	0.36	19.5

**Table 2. Percent recoveries of field test spikes for the NCASI method.**

Run	Average Concentration of Sample With Spike (ppm)	Average Concentration of Sample Without Spike (ppm)	Average Measured Spike (ppm)	Average Spike (ppm)	Percent Spike Recovery
2	48.48	37.52	10.96	14.16	77.4
3	45.52	31.37	14.16	13.72	103.1
4	37.62	31.04	6.58	13.46	48.9
5	40.77	27.94	12.83	13.87	92.5
6	38.40	27.34	11.06	13.76	80.3
7	37.78	25.56	12.22	13.94	87.7
Mean	41.43	30.13	11.30	13.82	81.6
Std. Deviation	4.56	4.25	2.60	0.23	18.5

Development and Validation of a Source Test Method for  
2,4-Toluene Diisocyanate

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**ABSTRACT**

Four isocyanates are listed for regulation in the Clean Air Act Amendments of 1990: hexamethylene-1,6 diisocyanate, methylene diphenyl diisocyanate, and 2,4-toluene diisocyanate, each of which is used in the production of polymers, and methyl isocyanate which is an intermediate in the manufacture of the insecticide carbaryl (i.e., Sevin®dust).

To support projected regulations, a study is under way to produce a source sampling and analysis method for the four pollutants cited above. In the procedure under development, the isocyanates are collected in an absorbing solution and derivatized with 1-(2-pyridyl)piperazine and analyzed by HPLC with UV detection. A system was developed in the laboratory to generate isocyanate atmospheres for optimization of sampling parameters and chromatographic conditions. The accuracy and precision of the method is determined in the field using train spiking and multiprobe sampling following the procedures outlined in EPA Method 301.

A field test of the isocyanate method, following EPA Method 301 procedures, was performed at a flexible foam manufacturer in the Greensboro-High Point, North Carolina area. The results were excellent, with analyte spike recoveries of 91% ± 6%. The method's limit of quantitation (LOQ) was determined to be 351 ng of TDI/M<sup>3</sup>.

**INTRODUCTION**

A class of compounds identified as isocyanates are contained in the list of 189 pollutants to be regulated by the Environmental Protection Agency under Title III of the Clean Air Act Amendments<sup>1</sup> (CAAA) of 1990. There are four isocyanates of interest in the CAAA; methyl isocyanate (MI), hexamethylene 1,6- diisocyanate (HDI), methylene diphenyl diisocyanate (MDI), and 2,4-toluene diisocyanate (TDI).

Isocyanates are used extensively throughout industry. A few examples of their use are the production of flexible foam products, synthetic rubber products, insecticides, enamel wire coatings, and in the pressed board industry. Foam materials alone are widely used for such diverse items as toys, bedding, seat cushions, packing material, flotation devices, and as sorbents in the environmental field. Because of their widespread use, isocyanates

possess the potential to affect many who are sensitive to this class of chemical compounds. Some of the adverse physiological effects associated with exposure to isocyanates are severe skin and eye irritations, eczema, nausea, and bronchial asthma.<sup>2</sup> An example of the concerns expressed about human exposure to the isocyanates is demonstrated by the NIOSH IDLH level (concentration considered Immediately Dangerous to Life or Health) for 2,4-toluene diisocyanate, which is listed at 10 ppm.<sup>3</sup>

Several critical problems exist when sampling for isocyanates. They polymerize in the presence of concentrated alkaline compounds, decompose upon exposure to water and alcohols, discolor upon exposure to sunlight, and form toxic gases, such as carbon monoxide and hydrogen cyanide, upon decomposition. Consequently, isocyanates must be collected rapidly and stabilized immediately with a derivatizing reagent to insure sample integrity.

The EPA's Source Methods Research Branch, in the Atmospheric Research and Exposure Assessment Laboratory, Research Triangle Park, North Carolina through a contract with Radian Corporation, Research Triangle Park, NC, has developed a method for the collection, identification, and measurement of one of the isocyanates of interest; 2,4-toluene diisocyanate. In this method, samples are collected at the source using a modified EPA Method 5 sampling train. Stack gas is withdrawn at a flow rate of 0.5 ft<sup>3</sup>/min. for approximately sixty minutes through a heated, glass-lined probe and into two impingers containing a solution of the derivatizing reagent, 1-(2-pyridyl)piperazine in toluene. The first impinger is fitted with a water-cooled condenser, on the outlet of the impinger, to minimize carryover of the organic solvent into the second impinger. The 2,4-toluene diisocyanate reacts with the derivatizing reagent to form a stable TDI/urea derivative. When sampling is completed, the probe and connecting glassware are rinsed with toluene and acetonitrile and the rinses are saved for laboratory analysis. Each impinger solution (TDI/urea derivative) is recovered separately and saved for laboratory analysis. All samples are stored in a cooler at 0 to 4° C until returned to the laboratory for analysis by High-Performance Liquid Chromatography (HPLC with UV detection). Quantitation is by a standards/retention time comparison procedure.

## *EXPERIMENTAL*

### Laboratory Evaluation

The laboratory study was initially set up to meet seven objectives for the four isocyanates of interest. However, midway through the laboratory study, budget constraints required the focus to be shifted to only one of the isocyanates of interest. After discussions with personnel in the EPA's Office of Air Quality Planning and Standards, it was decided to focus our efforts on 2,4-toluene diisocyanate. The seven objectives originally planned for all of the isocyanates were followed for TDI and are listed in Table 1. Some of the objectives were also met for the other isocyanates of interest and are also listed in Table 1.

## Derivative Formation

Efforts to form a stable isocyanate/urea derivative for all four isocyanates, using ethanol as the derivatizing reagent were only marginally successful. An absorption solution was prepared by adding 1 gram of KOH to 500 mL of 99.9% ethanol. Standard solutions of each of the isocyanates were prepared by adding the isocyanate directly to 5 mL each of the ethanol/KOH solution as follows: 30 mg of MDI; 10 uL of MI, HDI, and TDI. Solid derivatives for MDI, HDI, and TDI were obtained, but formation of a derivative for MI was unsuccessful. Chromatograms for the derivatized and underivatized isocyanates were compared. No chromatographic peaks were observed for MI or HDI either derivatized or underivatized, however, peaks were detected for TDI and MDI.

Previous work by Goldberg, et al.<sup>4</sup>, using 1-(2-pyridyl)piperazine as the derivatizing agent, investigated collecting ambient air samples in midget impingers. Since no current source method for isocyanates exists, the secondary amine, 1-(2-pyridyl)piperazine [1,2PP] was investigated as a possible alternative derivatizing reagent for ethanol. Using the 1,2PP as the derivatizing reagent resulted in the formation of solid derivatives for all of the isocyanates of interest. Each isocyanate was prepared in a separate 200 mL flask. Approximately 0.2 grams of TDI, HDI, MDI was added to separate solutions of 0.3 mL of 1,2PP and 10 mL of acetonitrile (ACN). The solutions were allowed to stand for 24 hours to insure enough time for the reaction to take place. Each derivative was then rinsed with 150 mL of distilled water and allowed to air dry before being redissolved with acetonitrile and brought to a standardized volume prior to analysis by HPLC. A derivative for the MI was prepared by transferring 100 uL of MI to 1 mL of ACN and adding 300 uL of 1,2PP. The solution was shaken for five minutes and then diluted 1:1000 for analysis by HPLC. A 1,2-PP solution was prepared as previously mentioned for blank analysis on the HPLC. Also, a solution of the 1,2-PP with MI, HDI, MDI, and TDI was prepared to determine the retention time of each derivative. The results were excellent, demonstrating that a mixture of the four isocyanates could be analyzed with good chromatographic separation and quantitation.

## Isocyanate Generator

An isocyanate atmosphere generator was constructed to provide a source of isocyanates as a simulated source, for testing within the laboratory. It is expected that this generator will be applicable to all four of the isocyanates listed in the CAAA, but for the reasons explained earlier the generator was tested only for TDI.

A modified Method 5 sampling train (without the in-line filter) was set up in the laboratory. Attached to the end of the probe was a piece of heated 0.5 inch quartz tubing with a stainless

steel tee and septum (for introduction of the isocyanate(s) standard). The temperature of the probe and quartz tubing were maintained at 120° C. Five impingers were connected in series for this study. The first impinger was a Greenberg-Smith impinger and the four following impingers were modified Greenberg-Smith impingers (straight stem - no tip). Room air was pulled through a charcoal scrubber into the heated quartz tubing and subsequently into two impingers containing the 1,2-PP absorbing solution. Following the two impingers containing the absorbing solution were one empty impinger (trap), a silica gel impinger, and an impinger containing charcoal (scrubber). A TDI standard in methylene chloride ( $\text{MeCl}_2$ ), prepared as described earlier, was introduced by a motor driven syringe pump, through the septum and into a heated air stream. Room air was sampled at a rate of 0.5  $\text{ft}^3/\text{min}$  for 40 minutes. This flow rate was chosen to test collection efficiencies at a flow rate expected to be used during the field testing. Cleanup and analysis procedures were as previously described, using toluene and ACN rinses and HPLC-UV analysis. Sample breakthrough, as measured by the recovery in the second impinger, was less than 8 percent. Mean recoveries for seven sample runs were 77 percent (see Table 2).

When the data in Table 2 was reevaluated, by eliminating the obvious outliers (Grubbs t-test for multiple outliers)<sup>5</sup>, the mean recovery is 98 +/- 15%. An obvious cause for the two outliers was not determined, since all operating parameters were standardized for the seven sample runs. As stated by Snedecor and Cochran in their chapter on regression analysis and outliers<sup>6</sup>, "when no explanation is found [for the outliers] the situation is perplexing. It is usually best to examine the conclusions obtained with the suspect (i) included, (ii) excluded. If these conclusions differ materially, as they sometimes do, it is well to note that either may be correct." Even though the Grubbs test for multiple outliers indicates that both of the outliers are suspect it is important to note that should one choose to include the suspect outliers, the recovery data would still be acceptable according to EPA Method 301 criteria.<sup>7</sup>

#### Method Validation

A field test of the method was performed in February, 1993, at a flexible foam manufacturer in the High Point, North Carolina area. A modified Method 5 sampling train (with a water-cooled condenser on the outlet of the first impinger) was used to collect source gas from the plant's process vent (see Figure 1). The sample gas stream was passed through a heated glass-lined/stainless steel probe and through two impingers containing the 1,2-PP absorbing solution, one empty impinger (carryover trap), one silica gel impinger, and one impinger containing charcoal (to trap any toluene vapors before they could enter the meter box). Sampling was non-isokinetic at 0.5  $\text{ft}^3/\text{min}$  for 60 minutes. Non-isokinetic sampling was performed since a presurvey indicated the analyte of

interest was present in the gas phase. Two of the quad trains for each sample run were spiked with a TDI derivatized standard (22.5 mg TDI/urea derivative in 15 mL of ACN). This standard spike was the equivalent of 8 mg of underivatized TDI, which was the amount indicated by the presurvey that we could expect to collect in sixty minutes of sampling. Impingers and other glassware used in the sampling train were rinsed first with toluene and then with ACN. Probe rinse and associated glassware rinses were combined with the contents of the first impinger for subsequent analysis by HPLC-UV. Toluene/acetonitrile rinses from the condenser and second and third impingers were also combined for HPLC analysis. Samples were kept on ice at 0 to 4° C until returned to the laboratory.

Operating parameters for the HPLC were as follows:

Instrument: Rainin HPXL delivery system with Waters  
710B WISP autosampler.  
Data System: Nelson 2600 (1 volt)  
Column: Zorbax ODS (4.6 mm ID x 25 cm)  
Mobile Phase: ACN/0.1M ammonium acetate buffer  
Gradient: 25:75 ACN/0.1M ammonium acetate buffer,  
pH 6.2, hold 2 min, then to 60:40 ACN/0.1M  
ammonium acetate buffer for 19.5 min.  
Detector Wavelength: 254 nm  
Flow Rate: 2 mL/min.

Results from the field test were excellent (see Table 3). The mean recovery of the spikes was 91 +/- 6%. Breakthrough, as measured by the recoveries in the second impingers, were all less than 2 percent, indicating near complete recovery in the first impinger. Background or emissions concentrations (as determined by analysis of the unspiked trains) ranged from 2000 ug/M<sup>3</sup> to 7700 ug/M<sup>3</sup>. The method's Limit of Quantitation (L<sub>Q</sub>) for TDI, calculated as outlined in EPA Method 301<sup>7</sup>, was determined to be 351 ng/M<sup>3</sup>. The L<sub>Q</sub> of the method is defined as ten times the standard deviation of the mean of the data set whereas the method Limit of Detection (L<sub>D</sub>) would be calculated as 3.3 times the standard deviation of the mean of the data set.

#### CONCLUSIONS

A method has been developed for the collection and analysis of TDI. Method validation procedures are still underway, but preliminary results from the first field test indicate that the method can be applied with a great degree of confidence to source emissions for TDI. Other isocyanate compounds (MI, MDI, HDI) have been or are being studied, and it is hoped that this method can be successfully applied to them as well. Current plans are for another field test in the near future, at another flexible foam manufacturer or other end user. Conditions not experienced in the sampling of source emissions during the first field test (i.e., higher humidity, particulate loadings, and/or warmer stack gas temperatures) will be investigated in the next field test.

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#### DISCLAIMER

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Table 1. Isocyanate Project Objectives

No.	Objective Description	MI	MDI	HDI	TDI
1	Find one derivatizing reagent to react rapidly with all four isocyanates	yes <sup>1</sup>	yes	yes	yes
2	Set up analytical HPLC method (for a single chromatographic run)	yes	yes	yes	yes
3	Develop instrument and method detection limits	no	yes	yes	yes
4	Determine spike recovery from derivatizing reagent	no	no	no	yes
5	construct an isocyanate generator	no	no	no	yes
6	Determine recoveries from spiked Method 5 train	no	no	no	yes
7	Field test of method and validation	no	no	no	yes

<sup>1</sup>- Yes indicates that objectives have been met. No indicates that an attempt has not been made to meet the objectives.

Table 2. Recoveries of Isocyanate (TDI) Spikes

Run No.	Spike Amount (ug)	Spike Recovery (ug)	Recovery (%)
1	2.5	3.05	122
2	2.5	0.60	24
3	2.5	2.30	92
4	2.5	0.65	26
5	2.5	2.13	85
6	2.5	2.53	101
7	2.5	2.23	89
Mean w/outliers			77 +/- 38
Mean wo/outliers			98 +/- 15

Table 3. Field Test Spike Recoveries

Sample Train Identification <sup>1</sup>	Spike Amount (ug)	Spike Recovery (ug)	Recovery (%)
1A	7828	7436	95
1B	7828	6654	85
2C	7828	6732	86
2D	7828	7280	93
3A	7828	6810	87
3B	7828	7280	93
4C	7828	7436	95
4D	7828	7593	97
5A	7828	6888	88
5B	7828	7436	95
6C	7828	7515	96
6D	7828	7671	98
7A	7828	7826	100
7B	7828	6575	84
8C	7828	6732	86
8D	7828	6419	82
Mean			91 +/- 6

<sup>1</sup>- Sample trains A&B are paired trains, as are sample trains C&D.

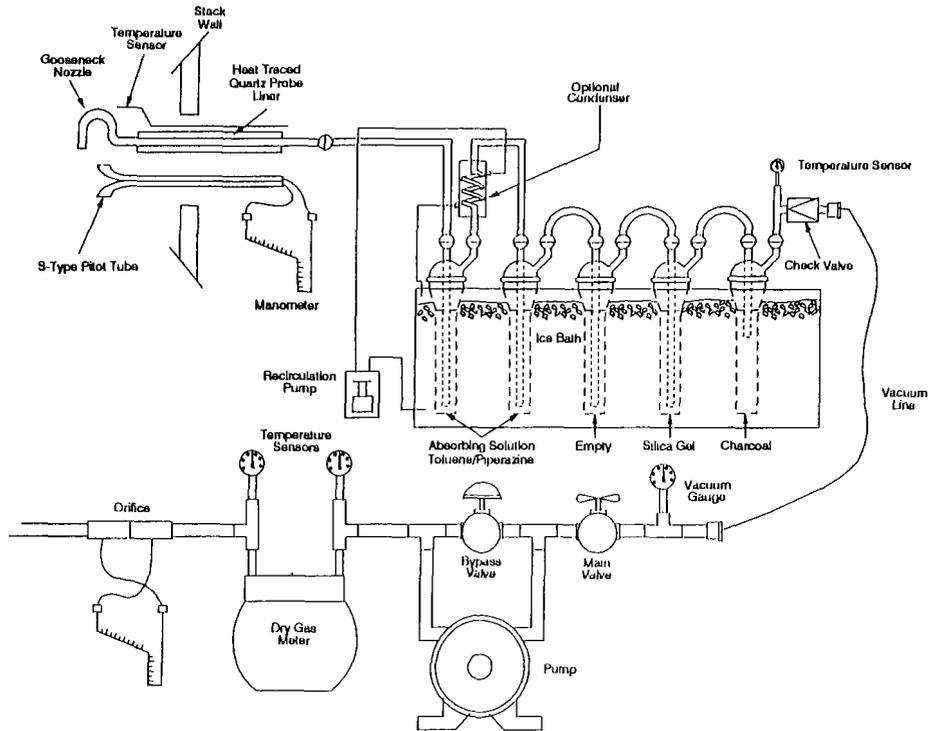


Figure 1. Isocyanate Sampling Train Configuration

SIMULTANEOUS SUPERCRITICAL EXTRACTION  
OF SEMIVOLATILE AND VOLATILE ORGANIC COMPOUNDS  
FROM XAD-2® SORBENT FOR AIR TOXICS AND  
STATIONARY SOURCE EMISSIONS

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This paper presents work performed to demonstrate that supercritical fluid extraction (SFE) could be used to extract large volumes of XAD-2® resins used for stationary source emissions sampling of air toxics. Basic SFE equipment capable of extracting 30 grams of sorbent was purchased and assembled. Supercritical fluid extraction conditions for extraction of source sampling resins were determined.

Average recoveries for three to five replicate extractions of XAD-2® analyzed in triplicate ranged from 32 to 162 percent. For 17 of 32 organic compounds tested, average recoveries ranged between 70 and 103 percent. Compounds that were quantitatively recovered include ethylbenzene, xylene, N-nitrosodi-n-butylamine, 2-methylnaphthalene, 2-nitroaniline, acenaphthylene, and dibenzofuran. Compounds that were not quantitatively recovered when present in low (0.1 to 0.5 mg) quantities include hexachloroethane, naphthalene, and 2,6-dichlorophenol. Results of the supercritical extraction experiments of XAD-2® resin are included in this paper.

## INTRODUCTION

The first step in analysis of air samples collected on XAD-2® resin involves separating the organic compounds from the matrix by Soxhlet extraction with methylene chloride. Solvent extraction techniques are sometimes time consuming, expensive, and methylene chloride is environmentally unfriendly. Supercritical fluid extraction could significantly simplify and increase the speed of the isolation process. Supercritical fluid extraction has the possibility of being fast, efficient, convenient, selective, quantitative, and low in cost after the initial investment in special equipment. Because the solvent strength of a supercritical fluid is directly related to the fluid density, the solvating ability of a supercritical fluid towards a particular organic compound can easily be modified by changing the extraction pressure and temperature. Supercritical fluids with different polarities are available and the polarity of a supercritical fluid can also be changed by using solvent modifiers. Using different extraction pressures, solvent modifiers, and solvents with varying polarities may be particularly valuable in achieving class-selective extractions.

Preliminary comparisons between SFE and Soxhlet extraction reported in the literature have shown that detection limits, reproducibility, and extraction efficiencies are comparable between the two techniques when small (1-2 g) sample sizes are extracted. Also, SFE is faster, produces an extract with fewer contaminants, and can be performed in the field. Supercritical fluids have shown potential in quantitatively extracting polynuclear aromatic hydrocarbons,<sup>1,2,3</sup> alkanes,<sup>3</sup> polychlorinated biphenyls,<sup>3</sup> pesticides,<sup>3</sup> halocarbons,<sup>3</sup> and polychlorinated dibenzo-p-dioxins<sup>4</sup> from XAD-2® in sample sizes much smaller than those required for stationary source emissions. Thus, if target compounds typically found in source samples could be quantitatively extracted from these resins using supercritical fluids, several advantages would be achieved. These include elimination of the use of methylene chloride (MeCl<sub>2</sub>), simultaneous sampling and analysis for volatile and semivolatile compounds, replicate analysis of samples for precision, and concentration of samples containing low concentrations of analytes. The objective of this work was to determine if SFE of large volumes of XAD-2® resins used for stationary source emissions sampling of air toxics by Method 0010<sup>5</sup> was feasible.

## EXPERIMENTAL PROCEDURES

### SFE Parameters Study

The SFE used: a. was capable of obtaining pressures up to 700 kilograms per square centimeter ( $\text{kg}/\text{cm}^2$ ), b. an intensifier pump that included an air input pressure regulator for accurate control of supercritical fluid output pressure and that was capable of providing supercritical fluid flows in the liters per minute range and c. an extraction cell. The extraction cell was assembled from a threaded preparative high performance liquid chromatographic (HPLC) column (30 mm by 15 cm) with Kel-F end fittings rated to  $350 \text{ kg}/\text{cm}^2$ . Supercritical fluid chromatographic (SFC) grade  $\text{CO}_2$  was used as the extraction fluid. A polar modifier, methanol (MeOH), was used, since some of the analytes were polar.

The XAD-2<sup>®</sup> was prepared following the procedures and quality control criteria in EPA 600/7-78-201.<sup>6</sup> Approximately 30 g of resin was packed into the extraction cell. The remaining space in the cell was filled with silane-treated glass beads using silanized glass wool to separate the XAD-2<sup>®</sup> and glass beads. The extraction cell was packed so that the supercritical fluid passed through the XAD-2<sup>®</sup> resin first and then through the glass wool and beads. Two spiking solutions were prepared with 32 organic compounds in MeOH. The compounds and the levels of each are shown in Table 1. The spiking solution was injected into the center of the resin using a gas-tight syringe.

After the extraction system was set up and checked, preliminary extractions using XAD-2<sup>®</sup> were performed to determine extraction conditions. All preliminary extracts were screened by GC/FID to provide immediate feedback. Later selected samples were analyzed by gas chromatography with mass spectrometry (GC/MS) detection.

Initially two extract collection procedures were tried, cryotrapping and collecting the extract in MeOH. The extract was collected in 2 to 5 mL of MeOH since MeOH was already present as the modifier. MeOH has a low freezing temperature ( $-95^\circ\text{C}$ ), and most of the analytes were soluble in MeOH. The collection vessel was a 40-mL vial and the fluid flow rate was adjusted to minimize loss of analytes due to aerosol formation. Flow rate was controlled using a flow restrictor. Different restrictors were evaluated including crimped nickel tubing (1/16-inch outer diameter) and various diameters of fused silica tubing (0.53, 0.1 and 0.05 mm inner diameter).

#### Recovery and Accuracy Studies

Once the extraction conditions were determined, ten SFEs were performed on XAD-2<sup>®</sup> to measure recovery and precision. Two extractions were performed on blank XAD-2<sup>®</sup>. Five replicate extractions were performed on XAD-2<sup>®</sup> at a low semivolatiles and high volatile organic compound concentration and three replicate extractions were performed at a high semivolatiles and low volatile organic compound concentration. Analysis of the supercritical extractions was by gas chromatography with a flame ionization detector (GC/FID). Each extract was analyzed in triplicate. Because relative and not absolute recovery values were required, the instrument was calibrated with a one-point standard containing each of the components. The one-point calibration standard represented the levels expected for 100 percent recovery of each compound. All results were compared to this one-point standard.

## RESULTS AND DISCUSSION

### SFE Parameters Study

For the first three experiments, the supercritical fluid extract was eluted through the cryotrap and then through a bubble trap. The cryotrap was a stainless steel loop submerged in frozen acetonitrile (ACN). The bubble trap contained MeOH and was immersed in an ice bath. The outlet of the cryotrap was submerged in the chilled MeOH. At the completion of the extraction, the cryotrap was rinsed with MeOH. Analysis of the MeOH rinse plus MeOH from the bubble trap showed that no analytes were present. Results from these three experiments indicated that material either was not deposited in the cryotrap/bubble trap or was not being effectively removed from the cryotrap/bubble trap. Therefore, the use of the cryotrap was discontinued since the spike was not detected in the cryotrap.

Additional experiments were performed using a collection system consisting of a midjet impinger containing 5 mL of MeOH. The supercritical fluid entered the impinger through a piece of 1/16-inch outer diameter nickel tubing. Decompression of the supercritical fluid was controlled by crimping the end of the nickel tubing. The crimped end of the nickel tubing was submerged in the MeOH solution. The impinger was immersed in a dewar containing a slush of MeOH and liquid argon. Acetonitrile and liquid argon were also evaluated as a low temperature collection trap bath in a single experiment to arrive at the MeOH-liquid argon low temperature bath.

TABLE 1. SUPERCRITICAL EXTRACTION RESULTS

Compound	Amount Spiked (mg)	Recovery <sup>a</sup> (%)	Amount Spiked (mg)	Recovery <sup>b</sup> (%)
<b>Volatile Compounds</b>				
Benzene and 1,2-Dichloroethane <sup>c</sup>	0.432	66.7 ± 11.5	3.600	82.8 ± 10.7
1,2-Dichloropropane and Dibromomethane <sup>c</sup>	0.701	76.8 ± 7.4	5.840	88.4 ± 12.9
Toluene and Trichloroethylene <sup>c</sup>	0.441	88.8 ± 10.2	3.680	88.3 ± 11.4
Chlorobenzene and 1,1,2-Trichloroethane <sup>c</sup>	0.489	86.2 ± 9.2	4.080	92.2 ± 10.1
Ethylbenzene	0.163	80.6 ± 15.3	1.360	92.3 ± 10.8
Xylene	0.163	82.1 ± 8.5	1.360	91.7 ± 11.6
1,1,2,2-Tetrachloroethane	0.307	85.7 ± 13.8	2.560	55.4 ± 16.2
<b>Semivolatile Compounds</b>				
Phenol and 2-Chlorophenol <sup>c</sup>	6.148	83.8 ± 11.5	0.647	31.8 ± 11.3
Hexachloroethane	1.596	87.1 ± 9.7	0.168	36.6 ± 5.5
Naphthalene	1.376	86.2 ± 8.3	0.145	162 ± 61.9
2,6-Dichlorophenol	1.611	74.5 ± 9.4	0.170	0.00 ± 0.0
N-Nitrosodi-n-butylamine	1.961	84.0 ± 10.2	0.206	80.0 ± 13.2
2-Methylnaphthalene	3.572	87.3 ± 8.8	0.376	100 ± 9.2
2-Nitroaniline	2.090	80.8 ± 19.0	0.220	95.5 ± 12.9
Acenaphthylene	1.581	83.5 ± 10.1	0.166	99.2 ± 11.8
3-Nitroaniline and Acenaphthene <sup>c</sup>	2.964	82.5 ± 10.1	0.312	90.4 ± 13.5
Dibenzofuran	1.429	82.3 ± 10.8	0.150	103 ± 10.6
1-Naphthylamine and 2,4-Dinitrotoluene <sup>c</sup>	2.789	88.2 ± 16.4	0.293	69.5 ± 15.0
1,2-Diphenylhydrazine and Diphenylamine <sup>c</sup>	3.572	81.8 ± 9.0	0.376	95.7 ± 12.0
Heptachlor Epoxide and Fluoranthene <sup>c</sup>	3.344	42.2 ± 5.3	0.352	53.2 ± 12.9
DDE	1.566	66.3 ± 7.5	0.165	137 ± 35.3
DDD	2.090	60.1 ± 7.2	0.220	70.4 ± 9.6
Endosulfan Sulfate	1.657	68.1 ± 8.9	0.174	94.9 ± 13.1

<sup>a</sup> Average of three replicate extractions analyzed in triplicate (n=9).

<sup>b</sup> Average of five replicate extractions analyzed in triplicate (n=15).

<sup>c</sup> Compounds coeluted on GC/FID.

The crimped nickel tubing allowed a flow rate of 28.57 mL/min of gaseous CO<sub>2</sub>. This flow was estimated to be about 30  $\mu$ L/min of supercritical fluid. Because the extraction vessel was so large, a flow rate of 1 mL per minute of supercritical fluid was needed to provide reasonable extraction times (less than two to three hours per sample). Reproducible control of the flow rate by crimping the nickel tubing was not achievable so various diameters of fused silica tubing were evaluated.

The 0.53 mm inner diameter fused silica resulted in a flow rate of 5.6 L/min of gaseous CO<sub>2</sub>. This rate was estimated to be about 6 mL/min of supercritical fluid which was too high so no extractions were performed using the 0.53 mm ID fused silica. The 0.05 mm ID fused silica provided a flow rate of 570 mL/min of gaseous CO<sub>2</sub>. This flow rate was still too slow so a practical internal diameter of fused silica to use for extracting 30 g of XAD-2<sup>®</sup> was estimated to be 0.1 mm.

#### Recovery and Accuracy Studies

Recoveries for the triplicate and quintuplicate replicate extraction studies are reported in Table 1. Average recoveries for the volatile compounds ranged from 55 to 92 percent. Only benzene/1,2-dichloroethane in the low (0.1 to 0.5 mg) volatile spike and 1,1,2,2-tetrachloroethane in the high (1 to 4 mg) volatile spike had recoveries less than 70 percent.

Average recoveries for the semivolatile compounds ranged from 0 to 162 percent. For the high (> 1 mg) semivolatile spike, average recoveries ranged from 75 to 91 percent for all of the compounds except for heptachlor epoxide/fluoranthene, DDE, DDD, and endosulfan sulfate. These four compounds elute at the end of the chromatogram where the column temperature program is increasing and the column liquid stationary phase begins to bleed into the detector. The rising baseline from the bleeding stationary phase interferes with the integration and quantitation of these peaks.

For the low (< 1 mg) semivolatile spike, average recoveries range from 70 to 103 percent for all of the compounds except phenol/2-chlorophenol, hexachloroethane, naphthalene, 2,6-dichlorophenol, 1-naphthylamine/2,4-dinitrotoluene, heptachlor epoxide/fluoranthene, and DDE. Several of these compounds, such as phenol/2-chlorophenol and 2,6-dichlorophenol, are polar. Supercritical CO<sub>2</sub> sometimes does not extract polar materials as efficiently as it extracts nonpolar materials. Other compounds, such as hexachloroethane, have a high instrument detection limit (IDL) when using a flame ionization detector.

In Table 2, the total variance is separated among three factors: spiking level, extraction replicate, and analytical replicate. For DDD, the variance in the analytical replicate contributes 19% of the total variance. A high contribution to the variance from the analysis was expected from this compound because of the difficulties in integrating the peak reproducibly due to the column bleed from the temperature program and MeOH solvent used. Except for dibenzofuran, and phenol/2-chlorophenol, the major contributor to the total variance is the variance from the replicate extractions.

#### CONCLUSIONS

The study demonstrated that large volumes of XAD-2<sup>®</sup> could be extracted for volatile and semivolatile organic compounds by SFE. SFE resulted in quantitative recoveries for 17 out of 32 of the test compounds spiked onto 30 grams of XAD-2<sup>®</sup>. The average recoveries for these 17 compounds ranged from 70 to 103 percent. Recoveries for DDE (1.566 mg), DDD (2.090 mg), endosulfan sulfate (1.657 mg), 1,1,2,2-tetrachloroethane (2.560 mg), hexachloroethane (0.168 mg), and 2,6-dichlorophenol (0.170 mg) spiked on 30 g of XAD-2<sup>®</sup> were less than 70 percent. Recoveries for the following coeluting compound pairs spiked on 30 g of XAD-2<sup>®</sup> were less than 70 percent: benzene (0.173)/1,2-dichloroethane (0.259 mg); heptachlor epoxide (1.550)/fluoranthene (1.794 mg); phenol (0.244)/2-chlorophenol (0.403 mg); 1-naphthylamine (0.154)/2,4-dinitrotoluene (0.139 mg); and heptachlor epoxide (0.163)/fluoranthene (0.189 mg).

Recoveries of hexachloroethane and chlorobenzene/1,1,2-trichloroethane from 30 grams of XAD-2<sup>®</sup> were comparable at spike levels of 1 to 3 mg between supercritical fluid and Soxhlet extraction. Recovery for 0.145 mg of naphthalene spiked on 30 g of XAD-2<sup>®</sup> was greater than 130 percent because the background contamination of naphthalene in the XAD-2<sup>®</sup> was significant at this spiking level (11.8% of the spiked amount or 0.017 mg of naphthalene was detected in the XAD-2<sup>®</sup> blank). Recovery of 0.165 mg of DDE spiked on 30 g of XAD-2<sup>®</sup> was greater than 130 percent because of challenges in accurately integrating the DDE peak due to the column bleed.

Table 2. Determination of Source of Total Variance for Representative Compounds

Compound	Spiking Level		Extraction			Analytical	
	% of Total Variance	Prob of > F	% of Total Variance	Prob of > F	% of Total Variance	Prob of > F	
<b>Semivolatile</b>							
Naphthalene	25.6378	0.0001 *	73.8342	0.0001 *	0.5279	---	
Dibenzofuran	51.1728	0.0001 *	40.7863	0.0001 *	8.0409	---	
DDD	16.7624	0.0003 *	64.3577	0.0001 *	18.8799	---	
Phenol/2-Chlorophenol	87.3387	0.0001 *	10.1826	0.0001 *	2.4787	---	
<b>Volatile</b>							
Xylene	0.0000	0.0001 *	96.7069	0.0001 *	3.2931	---	
Benzene/1,2-DCEA	32.2888	0.0001 *	60.298	0.0001 *	7.4133	---	
1,2-DCPA/DBM	3.489	0.0001 *	95.3676	0.0001 *	1.1434	---	

\* Highly significant at the 99% confidence level

Several additional objectives can be pursued including optimization of SFE conditions for extracting stationary source samples collected on resins, design of a sampling cartridge that is amenable to SFE sample recovery and stationary source sampling, evaluation of SFE methods on actual source samples collected at an air toxic emissions or similar site, evaluation of the use of SFE to purify source sampling resins prior to field sampling, extension of current source sampling methods for collection of larger less volatile compounds and possibly thermally labile compounds by using supercritical fluid chromatography mass spectrometry (SFC/MS) to separate the analytes prior to detection and to solve coelution problems, and additional evaluation of SFE for extracting source samples from Tenax® as used in Method 0030.<sup>5</sup>

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# AN INVESTIGATION OF PROCESS MASS SPECTROSCOPY AS A CONTINUOUS EMISSION ANALYZER FOR STATIONARY SOURCES

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## ABSTRACT

In January 1993, Entropy Environmentalists, Inc. (Entropy) conducted a feasibility study employing a process mass spectrometer to measure hazardous air pollutant emissions from stationary sources. Testing was conducted at a small coal-fired boiler in conjunction with a Fourier transform infrared spectroscopy (FTIR) field validation test, and was supported by the Emission Measurement Branch (U.S. EPA/OAQPS). Mass spectroscopy was evaluated at the simplest level, without separation of the constituent gases and without specialized software. Presented in this paper are the results of this study and recommendations for increasing the effectiveness this methodology.

## INTRODUCTION

Title III of the Clean Air Act Amendments (CAAA) defines 189 hazardous air pollutants (HAP's) which industrial facilities are required to characterize, quantify and ultimately reduce. Due to the large number of compounds, and the time constraints for emissions compliance, sampling and analytical techniques which provide results in a timely fashion are in great need. In the past, conventional sampling methods have been employed. These methods often require large testing crews, and are often compound or functional group specific. In addition, these methods are time consuming, sometimes having two to three week turn around times for analytical results. For these reasons, instrumental methods having the capability to both identify and quantify multicomponent HAP mixtures at near real time conditions are being examined. Mass spectrometry (MS) is one such instrumental technique that has the qualifications for continuous emission monitoring from stationary sources.

The purpose of this study was to examine the following aspects of direct MS monitoring of HAP emissions:

- Effectiveness in gathering qualitative data.
- Limitations imposed by large non-HAP effluent constituents.
- Effectiveness of "process" MS software in interpreting mass spectra of multicomponent mixtures.
- Calibration techniques.
- Quantitative accuracy.

## EXPERIMENTAL

### Process Description and Sample Location

The emissions testing program was performed at a small coal-fired steam generation plant with an approximate heat input of 68 Mbtu/hr. At this plant, bituminous coal is pulverized and blown into the combustion chamber by fans that provide simultaneous suspension and combustion of the coal. The combustion gases and particulate matter exiting the boiler pass through an air preheater, baghouse, and an induced draft fan before being exhausted to the atmosphere via a stack. Sampling was performed at the baghouse outlet. The mobile laboratory housing the mass spectrometer and the FTIR spectrometer was located within 50 feet of the outlet location.

### Sampling System

An extractive gas sampling system was employed to provide sample to the analytical instrumentation. This system employed a Type 316 stainless steel probe, a Balston® filter, a Teflon® line and a pump, all heated to approximately 250°F. The sampling system transports the flue gas sample to the gas conditioning equipment and MS/FTIR systems located in Entropy's mobile laboratory. Velocity traverses were conducted to find the point in the duct of average flow rate. These were conducted at the same time as the moisture determinations. All sampling was conducted at a single point and was non-isokinetic. In addition to the MS/FTIR instrumentation, continuous emission monitors (CEMs) were employed on-site to verify the carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>), and oxygen (O<sub>2</sub>) concentrations.

Two different types of samples were examined with the MS:

- Hot/wet, or unconditioned sample, which is considered more likely than conditioned samples to represent the actual flue gas composition. Only particulate matter is intentionally removed from the gas in this type of sample.
- Condenser sample, which a standard Peltier dryer system was used to cool the gas stream to approximately 3°C. The resulting condensate was removed from the dryer with peristaltic pumps. This conditioning technique is known to leave the concentrations of inorganic and highly volatile compounds very near the (dry-basis) stack concentrations.

A heated distribution manifold within the mobile laboratory was used to monitor and control sample gas flow to the MS/FTIR instrumentation. Mass spectra were taken in conjunction with FTIR spectra from both hot/wet and condenser flue gas samples.

### Analytical System

The MS system employed for these tests was a Leybold Inficon, 200 atomic mass unit (AMU), Transpector H200M Quadrupole Mass Spectrometer System. The unit consists of five main parts: an ion source, a quadrupole mass filter, an ion detector, a vacuum pump, and a data acquisition system. Such instruments function by ionizing the molecules in the sample and injecting them onto the axis of a combined radio-frequency/constant quadrupole electric field. As the quadrupole field is ramped and modulated, ion fragments of only a particular charge-to-mass ratio maintain stable trajectories as they pass through the quadrupole field, where they are detected on-axis.

This particular instrument is most commonly used in residual gas analysis, where only a few compounds exist in the gas mixture. For this reason, the data acquisition software typically provides only minimal spectral manipulation capabilities. The Transpector was chosen for this testing since its small size and ruggedness allowed for table mounting in Entropy's mobile laboratory.

The Transpector MS system was positioned in Entropy's mobile laboratory at a point directly after the gas conditioning manifold. The MS system was maintained at a temperature just above 100°C to prevent sample condensation; higher temperatures could not be maintained without damaging certain electronics components. Sample was drawn through a tee in the FTIR absorption cell sample delivery line, a variable leak-rate valve (needle valve), and into the MS system by a combination of rough and turbo pumps (pumping speed approximately 40 L/sec). Figure 1 illustrates the sample gas delivery schematic from the source to the instrumentation.

### Dynamic Spiking

Cylinders containing up to five HAP's at concentrations of approximately 50 parts per million (ppm) diluted in nitrogen were prepared for Entropy by Scott Specialty Gases for this test. These "spike gases" were introduced to the sampling system through a zero to five liter-per-minute (lpm) mass flow meter. The heated outlet of the flow meter was connected to the sampling system via a tee located at the inlet of a 1 micron Balston particulate filter (initial particulate filter depicted in Figure 1), which was installed at the outlet of the probe. A 100-foot length of 3/8-inch (O.D) Teflon sample line connected the filter to the sample pump located within the mobile laboratory. All exposed unions were wrapped with heat tape and insulation to prevent condensation of the gases. A calibrated orifice located at the outlet of the secondary particulate filter was used to measure the total flow of the sample at the distribution manifold. The five-to-one spike dilution factor was maintained by controlling the spike and total sample flow rates.

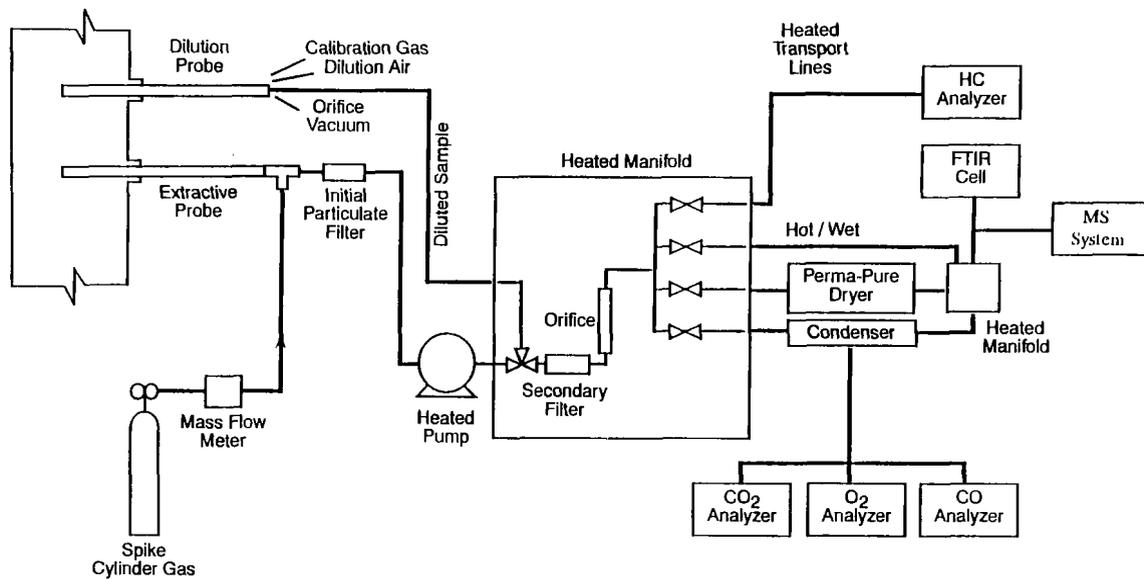


Figure 1. Simplified Schematic of the MS/FTIR Direct Gas Phase Sample Delivery System.

### Mass Spectral Collection

At the beginning of each day of the field test, the MS was manually "tuned" with perfluorotributylamine [CF<sub>3</sub>(CF<sub>2</sub>)<sub>3</sub>]<sub>3</sub>N (PFTBA). This volatile compound was loaded into a small valved ampule, which was permanently mounted at the sample inlet. These daily adjustments of the instrument were made to obtain characteristic mass fragments from the PFTBA over a large mass range, ensuring relatively constant mass fragmentation patterns for other sample molecules. Background spectra were collected on all testing days by evacuating the system through the heated sample distribution manifold. These spectra were examined for evidence of contaminants.

Mass spectra of gases in the FTIR sample cell were collected as follows. At a sample delivery pressure of one atmosphere, the total pressure in the MS system was adjusted to between  $1 \times 10^{-5}$  to  $3 \times 10^{-5}$  Torr by means of the variable leak valve. The 20 to 200 AMU range was then scanned; 20 data points per AMU at a nominal resolution of 1 AMU were collected. The scan time was 2.8 seconds (0.8 milliseconds per data point).

At the completion of the scan, peak areas for each 1 AMU segment were calculated and stored to disk. The software allowed such data files to be generated either as single spectral representations, or as multiple sub-files of spectra collected consecutively over a specified time period. In the latter case, which was selected for this testing, data were automatically generated at one minute intervals.

The indicated MS system pressure was observed to vary from spectrum to spectrum. Several possible causes exist for this instability, including the fact that the sample inlet pressure varied as the FTIR absorption cell was alternately filled with sample and then evacuated. However, it is also possible that surface effects of water and other major effluent constituents, heightened by the relatively low temperature of the quadrupole structure, played some role in the observed pressure fluctuations.

During the first few days of the test, the instrument was accidentally vented several times, requiring replacement of the filament. Due to this problem, data for most of the hot/wet sampling is unavailable. An "uninterruptable" power source was installed to power the instrument's vacuum pumps, which prevented recurrence of this problem.

### Data Analysis - Qualitative

The mass spectra recorded with the instrument were extremely complex, particularly at masses less than 50 AMU. The original software package supplied with the instrument was found inadequate for performing the spectral subtractions and other manipulations required for handling such spectra. Therefore, spectral files generated in the field were converted to a format compatible with a more sophisticated software package available from the same manufacturer.

Due to the complexity of the spectra, initial data examinations focussed on identification of the spiked compounds present in the sample. Only those compounds exhibiting strong ion peaks higher than 50 AMU were investigated, since the majority of large peaks belonging to the stack effluent constituents fall at masses below this level, and tend to interfere strongly with the low mass spike compound fragments. Additional interferences between the spike compounds themselves were also encountered, even at the higher AMU values. In order to quantify these compounds, fragmentation ions unique to individual compounds in the spike cylinders were sought. Some of the mass fragments were typically not the strongest in a compound's mass spectrum, and often represented a very small peak near the detection limit of the instrument. Spectra of the pure spike materials were compared to single-component spectra, obtained from the National Institute of Standards and Technology, in order to identify the parent molecular species.

### Data Analysis - Quantitative

For those compounds identified qualitatively, approximate quantification of gas phase concentrations were performed as follows. Reference spectra for pure compounds were recorded from existing 50 ppm gas standards prepared by Scott Specialty Gases. As mentioned above, the MS system total pressure was not constant for all the sample spectra. To account for possible effects of these variations, the reference spectra were recorded at the same MS system pressure as that observed when the sample spectrum of interest was recorded. A response factor was generated for a selected ion peak of each compound by dividing the observed reference ion peak area by the compound's reference concentration. Concentrations of the compounds in spiked samples were then calculated by dividing the observed sample ion peak areas by the response factors.

### RESULTS

The following Tables compare sample concentrations derived from the mass spectrometer data to those obtained from spike/sample flow ratios. Only compounds which could be quantified are reported. Due to the complexity of the results from FTIR validation testing, FTIR data are not presented. However, those compounds marked with an asterisk denote compounds which were not validated for the FTIR during the course of this test program. The data presented are derived mainly from the condenser samples, which were generally recorded over longer time intervals, and at lower water concentrations than the corresponding hot/wet data. Considering the degree of spectral interference between spikes and stack gas, the results for these compounds are in fair agreement with the expected concentrations.

TABLE 1.  
CYLINDER NO. 2 RESULTS  
CONDENSER

Sample	Compound	Mass Spectrometer		Expected Concentration
		Pressure (10 <sup>4</sup> Torr)	Concentration (ppm)	
GCS#2	Hexane	24	11.0	9.9
	Methylene Chloride*	24	4.5	10.0
	p-Xylene	24	11.0	10.0

TABLE 2.  
CYLINDER NO. 4 RESULTS  
CONDENSER

Sample	Compound	Mass Spectrometer		Expected Concentration (ppm)
		Pressure (10 <sup>4</sup> Torr)	Concentration (ppm)	
GCS#4	Isooctane	17	9.0	10.0
	Carbon Disulfide*	17	7.0	9.7
	m-Xylene	17	1.0	10.0

TABLE 3.  
CYLINDER NO. 7 RESULTS  
CONDENSER

Sample	Compound	Mass Spectrometer		Expected Concentration (ppm)
		Pressure (10 <sup>4</sup> Torr)	Concentration (ppm)	
GCS#7	Acrylonitrile*	10	14.0	10.0
	Allyl Chloride	10	2.0	10.2
	Ethyl Benzene	10	9.0	10.0

\* Denotes compounds not meeting EPA Method 301 criteria for FTIR validation

TABLE 4.  
CYLINDER NO. 9 RESULTS  
CONDENSER

Sample	Compound	Mass Spectrometer		Expected Concentration (ppm)
		Pressure (10 <sup>4</sup> Torr)	Concentration	
GCS#9	Methyl Tertiary Butyl Ether (MTBE)*	12	4.5	9.6
	Trichloromethane* (Chloroform)	12	9.0	9.7
	Cumene	12	4.5	10.0

TABLE 5.  
CYLINDER NO. 11 RESULTS  
CONDENSER

Sample	Compound	Mass Spectrometer		Expected Concentration (ppm)
		Pressure (10 <sup>4</sup> Torr)	Concentration (ppm)	
GCS#11	Styrene	14	3.0	9.6
	1,2-Dichloropropane	14	9.0	8.2
	Trichloroethylene	14	5.5	9.5

TABLE 6.  
HOT/WET  
AVERAGE CONCENTRATION

Sample	Compound	Mass spectrometer		Expected Concentration (ppm)
		Pressure (10 <sup>4</sup> Torr)	Concentration (ppm)	
GHS#11	Styrene*	14	15.0	10.8
	1,2-Dichloropropane	14	6.0	10.4
	Trichloroethylene	14	6.5	9.6

\* Denotes compounds not meeting EPA Method 301 criteria for FTIR validation

## CONCLUSIONS

In this study, simple mass spectrometry was found to provide useful quantitative and qualitative concentration data, even in a complicated combustion matrix. The main interfering compounds are (ion masses in parentheses) H<sub>2</sub>O (18), CO, N<sub>2</sub> (28), NO (30), O<sub>2</sub> (32), CO<sub>2</sub> (44), and SO<sub>2</sub> (64). These ion peaks dominate the mass spectra, along with their doubly and triply ionized species. However, the spectral interferences from these compounds do not present an insurmountable problem, since they appear primarily below 50 AMU. Spectra of particular HAP compounds, introduced as spikes, were clearly detectable at higher mass levels, despite spectral overlap from the stack matrix.

The applicability of the technique in HAP emission measurements applications could be enhanced by a number of possible developments, including the following:

- Provisions in the system's software for handling spectral interferences from high-concentration sample constituents.
- Increase of the quadrupole structure's temperature (100°C in this instance), to combat thermal drifts, which were sometimes noticed in high mass peak positions and intensities, and to lower background PFTBA and H<sub>2</sub>O levels.
- Provisions for stable sample pressure.
- Development of accurate quantitative reference spectra for target compounds for typical operating conditions.

Mass spectrometry could also prove to be extremely powerful in conjunction with other analytical methods. For instance, MS data could facilitate infrared analyses of heavy compounds, which possess relatively broad and uncharacteristic infrared absorption bands, but which may exhibit strong ion peaks in the relatively sparse high mass range.

## **GAS PHASE FTIR SPECTROMETRY AS A METHOD OF MEASURING HAZARDOUS AIR POLLUTANT EMISSIONS**

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### **ABSTRACT**

Entropy Environmentalists, Inc., (Entropy) conducted a field test using FTIR spectrometry to measure hazardous air pollutants (HAPs) emitted from a coal-fired boiler facility. Two techniques were employed: (1) introduction of extracted gases directly to the FTIR absorption cell and (2) sample concentration using Tenax followed by thermal desorption into the cell. Spiking experiments with HAP compounds were performed using each technique. Spectra were analyzed to measure spike recovery rates and to determine reproducibility of results.

### **INTRODUCTION**

The test described in this paper is part of the Environmental Protection Agency's (EPA) FTIR Method Development project. The purpose of the project is to develop a method to detect and quantify compounds listed in Title III of the Clean Air Act Amendments (CAAA). Prior to this test, Entropy developed a library of reference spectra, and performed screening tests at several industrial facilities representing a variety of source categories, including a coal-fired boiler.

The screening tests of the direct gas phase technique provided data on the performance and suitability of FTIR spectrometry for measuring the emission rates of HAPs. These tests helped determine sampling and analytical limitations, provided qualitative information on the emission stream composition, and allowed estimation of the mass emission rates for a number of HAPs and process locations.

At a coal-fired boiler, the usefulness of direct gas phase extraction FTIR for measuring HAP compounds at concentrations corresponding to 10 tons of emissions per year was found to be limited. This is because of the rather large effluent flow rates typical of such boilers; even small concentrations (i.e., sub ppm levels) of HAPs in the effluent output of the boiler can lead to potentially large yearly mass emissions. It was, therefore, necessary to develop a sample concentration technique before quantification of most HAPs by FTIR spectrometry could be attempted at such facilities. The screening test at the utility boiler also provided data on the interferent species and criteria pollutants that one would expect to encounter in a gas stream emitted from such a source. This information enabled Entropy to prepare for analyzing data before testing commenced.

The testing described in this paper represents a continuation of the method development project. The analyte spiking procedures of EPA Method 301 served as the model for experiments performed with 47 gas phase HAPs. Separate procedures were performed to test the direct extractive gas phase and the sample concentration/thermal desorption techniques. The goal was to determine the bias, precision, and range of the techniques. The data were analyzed to examine the suitability of the FTIR methods for testing of emissions from this type of source.

### **EXPERIMENTAL**

#### Process Description and Sample Point Location

Testing was performed at a bituminous coal-fired steam generating plant with an approximate heat input of 68 MBtu/hr. Bituminous coal is pulverized and blown into the combustion chamber by fans, providing simultaneous fuel suspension and combustion. The combustion gases and particulate exiting the boiler, pass through an air preheater, baghouse, and an induced draft (I.D.) fan before being exhausted to the atmosphere via a stack.

Measurements during this test were made at the outlet location of the baghouse. Direct gas extraction testing employed 100 feet of heated sample line to connect the sampling probe to the heated manifold in the FTIR truck. Concentrated samples were obtained through a port adjacent to where the direct extractive probe was inserted.

### Emission Sampling System

The FTIR-based method uses two different sampling techniques: (1) direct gas phase extraction and (2) sample concentration followed by thermal desorption. The direct gas phase sampling system extracts gas from the sample point and transports the sample to a mobile laboratory where sample conditioning and FTIR gas phase analyses are performed. The sample concentration system employs 10 grams of Tenax sorbent, which can trap some organic compounds from a large volume (typically 300 liters) of sample gas. These compounds are thermally desorbed into the smaller FTIR absorption cell volume (approximately 7 liters), providing a volumetric concentration which allows detection of some compounds below 1 ppm in the original sample. Components of the emission test systems prepared by Entropy for this testing are described below.

Direct Gas Extraction Gas was extracted through an 8-foot heated stainless steel probe. A heated Balston particulate filter rated at 1 micron was installed at the outlet of the sample probe. A 100-foot section of heated 3/8-inch O.D. Teflon® sample line connected the probe to the heated sample pump located inside the mobile laboratory. The temperature of the sampling system components was maintained at approximately 150°C. All components were constructed of Type 316 stainless steel, or Teflon®. Digital temperature controllers were used to monitor the temperature of the transport lines. All points of connection were wrapped with electric heat tape and insulated to ensure that there were no "cold spots" in the sampling system where condensation might occur. The sample pump provided approximately 16 L/min of sample gas flow. The heated sample flow manifold, located in the FTIR truck, included a secondary particulate filter and valves that allowed the operator to send the sample gas directly to the absorption cell or through one of the gas conditioning systems.

The extracted gas sample was treated in one of two ways. Sample sent directly to the FTIR cell was considered unconditioned, or "hot/wet." This sample is thought to be more representative of the effluent composition than conditioned samples. The gas stream could also be directed through a condenser to remove most of the water. The condenser employed a standard Peltier dryer to cool the gas stream to approximately 3°C. The resulting condensate was collected in two traps and removed from the conditioning system with peristaltic pumps. This technique is known to leave the concentrations of inorganic and highly volatile compounds very near to the stack concentrations (dry-basis). The condenser was tested in an effort to ascertain which HAPs can be reliably quantified using this system because the spectra are easier to interpret if water is removed.

Sample Concentration Four gas samples were collected simultaneously during each run using a quadrain assembly. Ten ft<sup>3</sup> of flue gas flowed through the Tenax cartridge over a sampling time of about 75 minutes.

Components of a single sampling train included a heated stainless steel probe, heated filter and glass casing, heated teflon connecting line, a stainless steel adsorbent trap in an ice bath, followed by two water-filled impingers, a knockout impinger, an impinger filled with silica gel, a sample pump, and a dry gas meter. All heated components were kept at a temperature above 120°C to ensure no condensation of water vapor within the system. The trap was a stainless steel U-shaped collection tube filled with 10 grams of Tenax sorbent and plugged at both ends with glass wool. Stainless steel was used for the construction of the adsorbent tubes because it gives a more uniform and more efficient heat transfer than glass.

Before use, the Tenax was precleaned to remove impurities that might desorb with any sample compounds collected. The packed tube was heated to 350°C while being treated with preheated nitrogen at 1 to 2 lpm. The heating and nitrogen flow were maintained for up to 18 hours. Cleaning the desorption tubes resulted in a decrease in impurity bands that Entropy has observed in spectra from the desorption of new, commercially precleaned Tenax.

After each sample collection, condensed water was removed before spectral analysis by blowing dry nitrogen through the Tenax while the sample tube was immersed in an ice bath. The collection tubes were then analyzed by thermal desorption-FTIR. The tubes were wrapped with heat tape and placed in a heating chamber. One end of the sample tube was connected to the inlet of the evacuated FTIR absorption cell. Gas samples were desorbed from the Tenax by heating to 250°C. A preheated stream of UPC grade nitrogen gas was passed through the adsorbent and into the FTIR absorption cell. Approximately 6 liters of nitrogen were

used to carry desorbed gases to the cell and to bring the total pressure of the FTIR sample to atmospheric pressure. The infrared absorption spectrum was then recorded. The purging process was repeated to verify that no evidence of additional sample desorption was noted in the infrared spectrum.

### Analytical System

The FTIR equipment employed in this test consisted of a medium-resolution interferometer, a heated infrared absorption cell, a liquid nitrogen cooled mercury cadmium telluride (MCT) broad band infrared detector, and a computer. The interferometer, detector, and computer were purchased from KVB/Analect, Inc., and comprise their base Model RFX-40 system. The nominal spectral resolution of the system is one wavenumber ( $1 \text{ cm}^{-1}$ ). Sample was contained in a variable path white cell, model 5-22 H, manufactured by Infrared Analysis, Inc. Heated jackets and temperature controllers were used to maintain a cell temperature of  $240^{\circ}\text{F}$ . The absorption path length was externally adjustable from about 2.2 to 24 meters. For the test, the path length was kept at 22 meters.

### Dynamic Spiking

Cylinders containing up to five HAPs at concentrations of approximately 50 (ppm) were prepared for Entropy by Scott Specialty Gases. The spike gases were introduced through the direct extractive gas sampling system using a mass flow meter capable of measuring flows in the range of zero to five liters per minute (lpm). Spike flow ratios were verified in two ways. First, CTS gas (100 ppm ethylene in nitrogen) was introduced through the mass flow meter and spike line to the gas sampling system. This was done prior to insertion of the probe in the sample port so that the CTS spike was mixed with ambient air. Analysis files, which had been previously prepared, were used to determine the concentration of ethylene in the resulting sample. Another method of verification used the  $\text{SF}_6$  tracer contained in each spike cylinder. Any spectrum of a spiked sample could be analyzed for the concentration of  $\text{SF}_6$ , which should have been approximately 0.2 ppm after dilution.

For testing with the sample concentration system, spike gas was directed through a mass flow meter. The measured flow of gas was passed through a heated coil to heat the spike gas and then introduced to the sample system at the inlet to the Method 5 particulate filter. The combined stream travelled through the cooled collection tube where compounds could be adsorbed onto the Tenax. The total gas flow was measured with the dry gas meter. Spiking rates were chosen to provide gas concentrations of approximately 500 ppb in the stack and about 20 ppm in the FTIR cell.

### Testing Procedures

For gas phase testing, a complete data set for a cylinder mixture included 24 samples, half spiked and half unspiked. The samples were collected consecutively, at about five minute intervals. Complete data sets of untreated, "hot/wet," samples were collected for all 11 cylinder mixtures. Complete data sets of samples treated with the condenser were collected for some cylinder mixtures and partial data sets of condenser treated samples were collected for the remaining cylinders. Within a set of 24 samples, data were collected in groups of four unspiked, followed by four spiked samples. Alternate groups of four samples were extracted until 24 spectra were obtained.

Single runs, with the sample concentration system, consisted of sampling  $10 \text{ ft}^3$  of gas simultaneously through the four Tenax cartridges of the quad-train assembly. All four probes were inserted in the same sampling port. The test runs were performed during the day and charged tubes were desorbed during the evening.

### Calculation of Expected Spike Concentrations

Analytical results for samples containing a known amount of spiked material were compared to results for unspiked samples. It should be stressed that no spectroscopic evidence of the spike compounds was found in the unspiked samples.

Expected concentrations of HAP spike materials in gas phase samples were calculated on the basis of flow rates measured during the field test. These flow rates were constantly maintained during the performance of the field testing for each HAP spiking group, and were verified to within 10% by spectroscopic analysis for the 1 ppm  $\text{SF}_6$  tracer gas component in each cylinder.

The value for the expected concentration from the gas phase sampling is given by:

$$C_{\text{exp}} = \left( \frac{\text{Flow}_{\text{spike}}}{\text{Flow}_{\text{total}}} \right) \times (C_{\text{cyl}})$$

where:

$C_{\text{exp}}$  is the expected gas spike concentration.

$\text{Flow}_{\text{spike}}$  is the measured flow rate for the spike gas.

$\text{Flow}_{\text{total}}$  is the measured flow rate for the spike gas plus the stack gas.

$C_{\text{cyl}}$  is the cylinder concentration of the spike compound.

Expected concentrations of HAP spike materials in concentrated samples were calculated on the basis of spike flow rates, total gas sample volumes, and sampling time measured during each run of the field test. These quantities were not always the same for each run involving a spiking compound group, and also varied for the two spiked sampling trains within each run. To allow use of the Method 301 statistical tests, it was necessary to introduce scaling factors designed to yield equal expected concentrations for all the trains and runs. These factors were taken into account in corrections to the observed spike concentrations.

The expected concentration in the sample concentration system is calculated in two steps. The first equation determines the amount of spike gas that is placed on the Tenax. It is given by:

$$\text{Vol}_{\text{spike}} = (T_{\text{spike}}) \times \left( 50 \frac{\text{cc}}{\text{min}} \right) \times \left( \frac{\text{L}}{1000 \text{ cc}} \right)$$

where:

$\text{Vol}_{\text{spike}}$  is the volume (in liters) of the spike gas flowed through the sampling system.

$T_{\text{spike}}$  is the length of time for sampling.

The value of 50 cc/min was the spike gas flow rate into the sample concentration system.

The expected concentration is then given by:

$$C_{\text{exp}} = \left( \frac{\text{Vol}_{\text{spike}}}{7.0 \text{ L}} \right) \times (C_{\text{cyl}})$$

where:

$C_{\text{exp}}$  is the expected concentration.

$C_{\text{cyl}}$  is the cylinder concentration of the spike gas.

7.0 liters is the volume of the FTIR cell.

#### Calculation of Observed Spike Compound Concentrations

The reported values were calculated using the Multicom program (Version 6), which is part of the KVB/Analect FX-70 software package. This program utilizes a calibration matrix created from a set of reference spectra. The program was employed to characterize the relation between known and calculated absorbance values of the reference spectra via least squares methods. The resulting matrix was then used to determine concentrations in the unknown mixtures. K-type calibration matrices were used to relate absorbance to concentration. Descriptions of this analytical technique can be found in the literature<sup>1,2</sup>.

Reference spectra for the K-matrix concentration determinations were de-resolved to  $1.0\text{ cm}^{-1}$  resolution from existing  $0.25\text{ cm}^{-1}$  resolution reference spectra. This was accomplished by truncating and re-apodizing the interferograms of single beam reference spectra and the corresponding background interferograms. The processed single beam spectra were recombined and converted to absorbance.

#### Preparation of Analysis Programs

To provide accurate quantitative results, K-matrix input must include absorbance values from a set of reference spectra which, added together, qualitatively resemble the appearance of the sample spectra. For this reason, all of the Multicomp analysis files included spectra representing interferant species and criteria pollutants present in the flue gas in addition to de-resolved reference spectra of HAPs used for analyte spiking experiments.

Prior to the actual field test, synthetic spectra were prepared using sample spectra that had been obtained during previous testing at a coal-fired boiler. K-matrix programs were then constructed which could adequately analyze the synthetic spectra. These analysis programs were found to serve as a useful starting point; all the finalized Multicomp routines are based on the programs prepared using the synthetic spectra.

Preparation of the synthetic spectra proceeded in the following stages. First, Entropy obtained a  $1\text{ cm}^{-1}$  reference spectrum of each cylinder mixture to be used in the analyte spiking experiments. Second, the cylinder spectra were scaled by a factor of 0.2 to simulate the anticipated dilution. Finally, a computer generated synthetic spectrum was created by adding a scaled cylinder spectrum to each of several sample spectra from the coal-fired boiler. This resulted in a set of synthetic spectra (for both "hot/wet" and condenser samples) representing simulated spiked samples in a stack matrix similar to what would be encountered during the spiking experiments.

#### **RESULTS AND DISCUSSION**

The spectral analysis programs were applied to all sample spectra. All spectra were visually compared to spectra of the spike cylinder gases to ensure that the resulting concentrations were physically reasonable and that no obvious spectral interferants had been omitted from the analytical programs. Statistical analysis of the data was carried out and compounds were evaluated based on the reproducibility of calculated spiked and unspiked results. A preliminary draft report summarizing the test results has been submitted to EPA, who will determine which compounds used in spiking experiments can be measured with the sampling techniques described in this paper.

Spectra and analytical programs involving compounds for which results were not reproducible were subject to further scrutiny. In many cases, improvements in the analytical results were achieved by adjustment of the spectral region and/or baseline subtraction technique employed in the Multicomp program. Following these adjustments, the statistical analysis was repeated. Correction of the programs often gave improved results. Table 1 presents calculated concentrations for ethylene dibromide, a compound that gave reproducible results, in spiked and unspiked samples. One data set is for untreated samples and the other data set is for samples treated with the condenser system.

Several generalizations may be made concerning the difficulty in measuring some species. A small number of compounds are simply not observable in the spectra of the direct gas samples delivered to the FTIR instrumentation. Examples of such compounds are ethylene oxide and propylene oxide; for these compounds, the observed spiked and unspiked concentrations differed only slightly. This may be due to heavy water spectral interference, losses in the sampling system, or a combination of both effects. It is also clear from visual inspection of the concentrated sample spectra that a large fraction of the spike compounds simply are not efficiently delivered to the FTIR sample cell. Compounds with low boiling points ( $< 50^{\circ}\text{C}$ ) are probably not adsorbed on Tenax.

There is evidence that a few compounds were consistently delivered by the gas phase sampling system, but the analytical results give consistently low concentrations. There are several possible systematic errors which could lead to such results, including (1) errors in the reference spectrum gas concentration, spike cylinder gas concentration, or both; (2) band intensity mismatch between reference spectra and sample spectra, caused by instrumental distortion or gas temperature mismatch between reference and sample spectra; and (3) a consistent loss of a certain fraction of the spike concentration in the sampling system.

Several compounds failed to give reproducible results because of spectral interference with particular spike or gas matrix species. Other compounds are different, in that visual inspection of the spectra indicates that the K-matrix analyses should successfully remove the interferences, but do not. The reasons for these failures are not fully understood, and are still being sought.

TABLE 1. Preliminary Results: Calculated Concentrations (in ppm) of Ethylene Dibromide for Spiked and Unspiked Untreated Samples and Samples Treated with the Condenser System.

Condenser		Unconditioned Samples	
SPIKED*	UNSPIKED	SPIKED	UNSPIKED
9.05	-1.14	6.52	-3.27
8.90	-1.05	6.52	-3.69
9.15	-0.99	6.51	-3.57
9.14	-1.31	6.53	-3.57
7.25	-1.45	6.84	-3.45
7.47	-1.48	6.91	-3.73
7.42	-1.47	6.84	-3.88
7.50	-1.47	6.77	-3.64
7.08	-1.46	6.58	-3.30
7.30	-1.52	6.52	-3.40
7.49	-1.54	6.48	-3.45
7.6	-1.55	6.44	-3.83
7.94	-1.37	6.62	-3.56

\* Expected concentration (spiked minus unspiked) is 10 ppm.

## CONCLUSIONS

The FTIR spectrometric analytical procedures described in this report have been applied to samples extracted from the flue gas stream of a coal-fired boiler. The results gave information which can be used to determine the utility of FTIR spectrometry for detecting and quantifying HAPs in a flue gas stream emitted from a coal-fired steam generation plant.

A total of 47 gas phase HAPs were introduced through the sampling systems and FTIR spectra were obtained for spiked and unspiked samples. The gas phase extractive system demonstrated utility for measuring a number of compounds in both "hot/wet" and condenser samples. The large amount of information obtained has been used to improve analysis procedures and to characterize limitations of each sampling technique for measuring particular compounds. The direct gas extraction and sample concentration techniques, when used in conjunction with FTIR spectrometry, provide versatile means of detecting and quantifying a large number of compounds from about 10 ppm to 500 ppb. Longer sampling times using the sample concentration technique, can easily provide improved detection limits for species that adhere to Tenax. The gas extraction technique can provide detection limits of close to 1 ppm, for many compounds, using the sampling system configuration described in this paper.

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## FIELD OBSERVATIONS OF COMPLIANCE MONITORING FOR ETHYLENE OXIDE EMISSIONS FROM HOSPITAL STERILIZERS

by

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### ABSTRACT

California Air Resources Board (CARB) Method 431, "Determination of Ethylene Oxide Emissions from Stationary Sources" specifies an on-site (direct) gas chromatographic procedure. This method has been applied and evaluated for compliance testing of hospital sterilizers with catalytic oxidation-, hydrolytic scrubber- and recovery-type control units. In several cases the control equipment required modification to accommodate the compliance tests. In several other cases the test method was modified in order to provide useful data. Proposed modifications to the test method will also be discussed including a Tedlar bag sampling procedure and an "inlet estimation" technique.

### INTRODUCTION

The work presented in this paper is a continuation of work presented at the 1992 EPA/A&WMA International Symposium on "Measurement of Toxic & Related Air Pollutants"<sup>1</sup>

An "Ethylene Oxide Airborne Toxic Control Measure (ATCM) for Sterilizers and Aerators" was adopted by CARB (17 CCR, Section 93108) on May 22, 1991. The ATCM requires control of ethylene oxide (EtO) emissions based on annual usage. The "control efficiency" is defined as the ethylene oxide mass or concentration reduction efficiency across a control device, as determined by CARB Test Method 431. The control efficiency is expressed as a percentage calculated across the control device using equation 1.

$$\frac{\Sigma \text{EtO in} - \Sigma \text{EtO out}}{\Sigma \text{EtO in}} \times 100 = \% \text{ Control Efficiency} \quad \text{Equation (1)}$$

CARB Method 431, "Determination of Ethylene Oxide Emissions from Stationary Sources", was based on work done by Radian Corporation for the United States Environmental Protection Agency (USEPA)<sup>2</sup>. The method is applicable to the determination of EtO emissions from sterilization chambers in pounds per sterilization cycle. The method requires direct interface GC/FID monitoring of EtO emissions. The ATCM requires that the inlet and outlet of the control device be sampled simultaneously during testing to measure the control efficiency. Volumetric flow of vented gas is monitored and total EtO emissions are calculated for the sterilization cycle using curves of flow and concentration determined over time. Modifications to Method 431 are now being considered by CARB, including options that allow the use of Tedlar bag sampling/laboratory analysis as well as an "inlet estimation" technique.

This paper will discuss the application of test procedures to the following types of control systems: catalytic oxidation- (cat-ox), hydrolytic scrubber-, and recovery-type. The discussion will primarily be a series of "problems" identified during actual testing.

CARB staff have worked closely with private source testing companies to adapt the test procedures to the specific types of control devices used in California. In particular, CARB acknowledges the cooperation of Mark Chips and Jeff Naus of Chips Environmental Consultants, Inc., whose work provided much of the information presented in this report.

## **DISCUSSION**

### **Catalytic Oxidation Control Systems**

In the typical operation of a cat-ox unit, the EtO laden exhaust air is pulled into the catalytic oxidizer through a prefilter by a pump, diluted with heated (300 F) ambient air and "burned" in the presence of a catalyst bed. Typical EtO inlet concentrations after dilution are about 3000 ppmv with typical EtO destruction efficiencies of 99.9%. Discussed below are several general observations regarding testing of cat-ox control units followed by manufacturer/design specific comments.

CARB Method 431 requires the use of Turbine-type or Roots-type meters as the method was intended primarily to measure emissions flow from acid scrubbers in cubic feet per minute. However, these types of flow measuring devices can only be used when the temperature of stack emissions is less than approximately 200°F. Thus the use of Turbine or Roots-type meters is not appropriate for emissions flow measurement from cat-ox units where the temperature of emission is typically between 350°F and 450°F. Instead, CARB Method 2 (type S pitot tube) should be used to determine stack gas velocity and volumetric flow rate of stacks greater than 12 inches in diameter. EPA Method 2C (standard type pitot tube) should be used where source stacks or ducts are less than 12 inches but greater than 4 inches in diameter. Typical cat-ox units operate at 50 and 100 scfm. The exhaust ducting of a typical control unit is 4 to 6 inches and occasionally up to 10 inches in diameter. The larger size ducting gives very low linear gas velocities (e.g., less than 10 ft./sec.) which are difficult to measure using standard pitot tube/manometer techniques. A practical solution is to reduce the diameter of the oversize stack to a temporary 4 inch stack during the test.

Volumetric flow of cat-ox units, corrected for temperature and pressure, is supposed to be controlled and constant, for example at 50 or 100 scfm, but up to 10% deviation has been observed during chamber evacuations. Thus the velocity measurements should be taken continuously or every 2 minutes to get an accurate total volume. While concentration measurements are obtained at both the inlet and outlet of the control unit, volumetric flow measurements need only be taken at the outlet (assume equal scfm at inlet and outlet).

Most of the EtO charged to the chamber of a sterilizer with cat-ox control unit will be delivered to the control unit during the first chamber exhaust. The length of this first evacuation from hospital sterilizers will typically range between 15 and 60 minutes followed by a series of air "washes" lasting from 1 to 2 hours. Accurate characterization of this short emission profile by on-site GC requires a sampling (GC injection) frequency of once every 2 minutes or less.

As stated above, sterilant gases are diluted with ambient air before contacting the catalytic bed of cat-ox units. This dilution is necessary for efficient oxidation of EtO as well

as to prevent damage to the catalytic bed. For the purpose of compliance testing the inlet gases should be sampled after dilution due to physical sampling difficulties before dilution as well as for safety of test personnel. If the control unit inlet total mass is measured by on-site GC or Tedlar bags rather than estimated, testers should have documented evidence that the inlet probe is placed such that the sampled gases are completely mixed (i.e., chamber exhaust and make-up air). Monitoring at locations where mixing is incomplete will produce erroneous results which could be either high or low, depending on the probe location. We have not seen any cat-ox units with manufacturer installed inlet probes. Testers have had to use their best judgement to position the inlet probe, which is normally a 1/4" copper tube centered in front of the catalytic bed. CARB proposed Test Method 422.103 describes procedures to document correct probe position. We have found that design modifications were necessary to perform valid inlet testing for Donaldson Company, Inc. and Autoclave Repair Specialists, Inc. (ARS) sterilization systems.

In addition to dilution with ambient air, 3M, Inc. sterilizer systems use a pulsed chamber exhaust flow to limit the feed rate of EtO to the cat-ox unit. This pulsed flow consists of cycling flow "on" for 5.66 seconds and "off" for 3.73 seconds for the first 16 minutes of the first evacuation. This pulsed exhaust flow presents an inlet sampling problem for on-site GC that is not encountered with integrated Tedlar bag sampling. On-site GC cannot sample fast enough to accurately characterize this pulsed emission profile. To minimize the problem of sampling a pulsed flow with on-site GC the sampling train at the inlet to the control unit was modified to include a 1 liter Greenburg Smith impinger that functioned as a mixing chamber for the sampled sterilizer exhaust gas prior to introduction into the GC analyzer. The mixing of the sampled gas smooths out the variable concentrations associated with the pulsed exhaust flow. Because the exhaust gases are adequately mixed by passing through the catalyst bed, the impinger is not necessary for sampling at the control unit outlet.

Many sterilization systems use water ring seal pumps to evacuate the chamber. Some EtO will be retained in the water as the sterilant gas passes through the pump. Depending on system design, water ring seal pumps can cause a shift in EtO emission from the initial chamber purge to the air washes and even into the aeration cycle. In particular this effect has been noted on MDT Castle, American Sterilizer Company (AMSCO), ARS and Banard and Associates control units. Testers need to be aware of these emission shifts and compensate appropriately during tests, especially when performing Tedlar bag sampling. If integrated Tedlar bag samples are collected, sampling should extend from the beginning of the first purge to at least 1 hour into aeration to compensate for emission shifts. In addition, the use of a continuous monitoring (e.g., FID) is strongly recommended to provide documentation that the bag sampling is representative of the emission curve. The inlet estimation technique should not be used with sterilization systems using water ring seal pumps.

Testers have speculated that ETO concentrations may, in many cases, be stratified in the exhaust duct flow from catalytic oxidation control units. Further investigation is necessary to better define this problem. However, if stratification does occur, some sort of sample averaging probe would be required to obtain valid test results.

Testers have observed performance problems which cause reduction of the destruction efficiency of catalytic bed of cat-ox units. The causes of these destruction efficiency problems are difficult to define precisely. Periodic overheating will cause the catalytic bed to lose activity with subsequent losses in EtO destruction efficiency. Improper installation has caused a number of catalysts to fail usually due to liquid water entering the bed and causing damage to the catalyst during startup. Also, channels or leaks can apparently develop in the beds. Using direct GC, a leak across the catalyst can usually be

identified in that inlet and outlet concentration "track" perfectly at a uniform efficiency (i.e. 3000 ppmv at the inlet gives 15 ppmv at the outlet and 1000 ppmv at the inlet gives 5 ppmv at the outlet; both pairs give exactly 99.5% efficiency in spite of the varying concentration). In contrast, for a functioning bed, the EtO destruction efficiency will vary with temperature (bed temperature changes during the cycle; EtO oxidation is exothermic) and EtO concentration, throughout the cycle. Routine testing, e.g. yearly, would help identify declining performance of cat-ox units.

#### **Acid Catalyzed Scrubbers**

Acid catalyzed scrubbers hydrolyze ethylene oxide into ethylene glycol by using an acid catalyst in solution with water. Typically, an acid catalyzed scrubber system is comprised of a packed tower, a reaction vessel, and a storage tank. After the sterilization cycle is completed, the sterilization chamber is exhausted and EtO is pumped to the packed tower where it comes into contact with an acidic water solution. Since EtO is water soluble, most of it is absorbed into the scrubber liquor which then enters a reaction vessel where the conversion to ethylene glycol is completed.

Revised Method 431 (422.103) allows the option to measure inlet concentrations (e.g., with bag sampling or by direct GC) instead of using the estimation technique. However, the concentration of EtO at the inlet of hydrolytic scrubber units will be approximately 27% and 100% by volume for systems using 12/88 EtO/Freon-12 and 100% EtO sterilant gases, respectively. Due to the safety concerns associated with the high inlet EtO concentrations, the estimation procedure is recommended.

The stability of ethylene oxide in hydrolytic scrubber unit emission matrix, in Tedlar bags, has not yet been demonstrated (by ARB staff). However, a report prepared by Coast to Coast Analytical Services, Inc.2 for the CARB suggested that acid mists in emissions from scrubber units might cause decomposition of EtO in whole air samples. The report also suggests that a sodium bicarbonate cartridge can be used to scrub acid mists from sample streams without affecting the EtO.

Sterilizers with scrubber units tend to have short primary evacuation times (e.g., 5 to 10 minutes). Thus the direct interface option should only be used to test hydrolytic scrubber units (inlet and outlet) if sample frequencies are 1 minute or less. Longer sampling frequencies may not adequately define the emission curves. For sterilizer systems using 12/88 sterilant gas, 1 minute GC sampling frequencies are not possible. Integrated Tedlar bag sampling is recommended.

Acidic cation exchange resins are often used to further reduce the emissions of EtO from acid scrubbers. The failure profile of these resin beds is unknown at this time.

#### **Recovery Units**

Recovery systems for EtO/CFC mixtures are a version of condensation/expansion refrigeration systems. At the conclusion of the sterilization cycle, the sterilant gas is drawn from the chamber through a desiccant bed or dehumidifier and is then compressed. The compressed and dehumidified sterilant gas reaches the condenser where it is cooled and condensed to liquid and delivered to recovery cylinders. Recovery cylinders, when full, are replaced and sent to reprocessing facilities. These systems are generally quite complex and require trained personnel to keep them operating. Sterilant recovery efficiencies are expected to be from 80 to 98 percent (for both EtO and CFC). To achieve the high control efficiencies (99.9%) required by the ATCM reclamation systems would have to include a control device

capable of complementing the recycling process. These recovery systems are too complex to discuss in detail in this report but several design and testing observations are listed below.

To date, only one recovery unit has been successfully compliance tested in California. The system, made by Joslyn Inc., recovers, under normal operating conditions, up to 98% of the EtO and CFC. Nonrecovered sterilant gas is routed to a dilute acid scrubber which has proven adequate even under upset conditions. Testing involved using inlet estimation technique and Tedlar bag sampling to collect the entire ~ & mission from the acid scrubber outlet for on-site GC analysis of EtO. Also, approximately 1.5 liters of EtO contaminated water are collected in a reservoir each cycle. This water is routed to a heated tank where the EtO is hydrolyzed before discharge of the water down the drain. Samples of water delivered to, and discharged from, the heated tank were collected and analyzed for EtO. The system is set up such that efficiency determination required averaging the results of multiple cycles (6 cycles).

Several other systems have been evaluated but not yet compliance tested. Donaldson Company, Inc. manufactures a unit which recovers most of the EtO and CFC. Nonrecovered sterilant gas is routed to a cat-ox control unit for further EtO abatement. No water is discharged to the drain from this system. Tests will likely consist of inlet estimation along with cat-ox unit inlet/outlet testing.

Medical Gas Industries Inc. (MGI) makes a system which reclaims most of the CFC and destroys the EtO. The sterilant gas passes through an acid scrubber to remove EtO before reclamation of the CFC. In addition, any nonrecovered gases pass through an acid cation exchange resin bed before emission to atmosphere. EtO contaminated water collected during the process is routed to the acid scrubber for abatement. The MGI system uses liquid nitrogen to condense the CFC. Tests will likely consist of inlet estimation with outlet testing at the resin bed exhaust and nitrogen vent line.

Again, in general, recovery systems are very complex and in many cases the installation will be site specific. Each recovery system should be carefully inspected during a pretest site visit to insure that it is testable. Subtle differences in piping can cause endless problems while attempting to run a test.

#### **"Inlet Estimation"**

The amount of EtO charged to the sterilization chamber, and delivered to the control unit, can be accurately calculated from weight loss in the charging cylinder/cartridge or from chamber pressure/volume relationships. This estimation procedure assumes that there is no loss of EtO to the chamber, chamber contents, transfer plumbing or pumps and that there are no significant leaks before the control unit. Following are several observations made regarding the application of this estimation technique.

Some sterilization systems add sterilant gas as needed to the chamber during the exposure stage because the chamber pressure may decrease slightly after initial pressurization. This addition of make-up gas would, if significant, invalidate the inlet estimation calculation as with existing systems it would be quite difficult to estimate the amount of make-up gas added. To minimize this problem, when using the inlet estimation technique, the test should be conducted with an empty chamber and the exposure stage should be aborted after no more than 10 minutes.

Since the estimation technique can only be used for empty chamber tests, an exposed chamber load will not be available if subsequent aeration tests are to be performed. There

must be an exposed load in the aerator for a valid test. Thus, an additional sterilization cycle with unaborted exposure stage would have to be run to provide the materials to be aerated. Furthermore, the inlet EtO concentrations must be physically measured with Tedlar bags or direct GC for aeration tests since estimation is not possible. Thus, where aeration tests must be conducted in addition to sterilizer tests, inlet estimation may not provide any time or cost benefit.

Use of the inlet estimation technique assumes that the composition of the sterilant gas is accurately defined and consistent in individual cylinders/cartridges. We have no information that these assumptions are correct. Thus, a sample from the gas cylinder(s) used during the test should be analyzed to verify the exact gas composition for the inlet estimate.

Accurate estimates rely on accurate volume measurements and calibrated pressure gauges. Thus, manufacturer's chamber volume specifications should always be double checked and system pressure monitoring devices should be evaluated for accuracy.

All sterilizers use some amount of water to activate the sterilization and there tends to be a residual puddle left in the chamber post-cycle. The amount of EtO in and the volume of this puddle are variable and unknown but are assumed to be insignificant .

As discussed previously, the inlet estimation technique should not be used with sterilization systems using water ring seal pumps.

#### **On-Site GC**

Several advantages and disadvantages of on-site GC are discussed below.

Direct sampling/analysis will identify a seriously non-complying unit within the first 10 minutes of testing. Thus, the system could be shut down immediately for repairs, minimizing the hazard associated with excess emissions.

On-site GC readily accommodates differences between control unit models. For example, the cycle timing and emission curve can vary dramatically between models made by different manufacturers. Also, some system configurations cause delayed release of sterilant gas to the control unit (e.g., water ring seal pumps) such that sampling intervals may need to be extended. With on-site GC, adjustments may be made during the test to produce more representative results.

At many hospitals, the control unit is not accessible from parking areas (i.e., with 150 foot heated lines to a parked GC-van). Thus, the GC must be physically moved to a location near the control unit, which may prove inconvenient. Also, adequate power may be difficult to get at some facilities.

Many testers feel that on-site GC is more expensive and more difficult than container sampling. In addition to the equipment required, performance of on-site GC requires that an experienced chemist be involved in the field operations.

#### **Tedlar Bag Sampling**

Several advantages and disadvantages of using Tedlar bag sampling for EtO compliance test are discussed below.

Tedlar bag sampling provides a true integrated sample over the duration of the emission, as opposed to direct GC which provides only a series of data points along the emission curve. However, some sources such as some acid scrubber configurations may not be suitable for bag sampling because both concentration and volumetric flow vary with time.

The Tedlar bag sampling procedure is potentially simpler and may be less expensive than direct GC. However, appropriate quality control, such as blank bag contamination and leak checks and field spikes and blanks must be incorporated into the test. Also, loss of samples due to bag breakage could present a problem.

Sampling with Tedlar bags must be planned carefully so that the entire emission curve is monitored. To provide documentation that the sampling is representative of the emission curve, it is strongly recommended that a continuous monitor (e.g., FID) be used along with the bag at the control unit inlet. Sampling times could then be modified as necessary to account for shifts in emissions.

Using CARB Method 422 procedures, a limit of detection of approximately 1 ppmv would be calculated for EtO samples collected in Tedlar bags and analyzed using the same GC analysis as used for direct GC. This level may not be low enough for regulatory purposes. Thus, some form of sample concentration may be necessary for analysis of EtO from Tedlar bag samples.

## CONCLUSION

As stated in the introduction, this paper has been a report of observations/problems encountered by private test groups during compliance testing for EtO emissions from hospital sterilizers. A goal of these tests was to adapt the test procedures for application to specific control unit types and configurations. In some cases the control equipment required modification to accommodate the tests. In other cases the test method was modified in order to provide useful data. In conclusion, it seems evident that sufficient differences exist between control units (manufacturer, model and site dependent) that close scrutiny is called for in application of the above described test procedures to obtain useful results.

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**EVALUATION OF POLYNUCLEAR AROMATIC HYDROCARBONS AND  
NITROGEN HETEROCYCLES IN THE STACK EFFLUENT OF  
ASPHALT PROCESSING PLANTS**

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**ABSTRACT**

The Connecticut Department of Environmental Protection (CT DEP) conducted stack effluent monitoring at several asphalt plants during 1991 and 1992. The samples were collected in accordance with US EPA SW846 Method 0010 and analyzed by high resolution gas chromatography/ high resolution mass spectroscopy (HRGC/HRMS).

The HRGC/HRMS methodology was developed by Triangle Laboratories, Inc. of Research Triangle Park, North Carolina to satisfy CT DEP's monitoring objectives. These objectives included determining the feasibility of monitoring and simultaneously analyzing for both polynuclear aromatic hydrocarbons (PAH) and nitrogen heterocycles (NHC) in asphalt plant stack samples. The list of target PAHs was developed by CT DEP to help better define its polynuclear aromatic hydrocarbon regulations.

The test results show that seven compounds from CT DEP's targeted list of PAH comprise 98-99% of the identified PAH emissions from asphalt plants. CT DEP reviewed data from oil and natural gas-fired batch operations as well as natural gas-fired batch and express plant operations. Comparisons of the results were made.

**INTRODUCTION**

The Connecticut Department of Environmental Protection (CT DEP) conducted stack emissions monitoring at several asphalt plants during 1991 and 1992. Two types of plants at the Balf Company were tested as part of a USEPA High Risk Point Source (HRPS) Study to determine qualitatively and quantitatively the PAH and NHC emitted from asphalt plants. CT DEP intended to use the PAH emissions data to regulate a specific source as well as support a revision of the existing, but inadequate PAH regulation.

At CT DEP's request two additional plants were tested. The Astec plant, a natural gas-fired, 4 ton/batch plant, was tested in fulfillment of a condition written into its permit to construct and operate. The other plant, Tilcon, a 5 ton/batch plant, agreed to be tested at the request of the department. For testing purposes, Tilcon temporarily converted to its backup fuel, No. 2 oil. Connecticut has a wide variety of asphalt plants. The majority of Connecticut's 45 plants burn No. 2 oil with natural gas backup. The newer facilities are required to burn natural gas with No. 2 oil backup. The plants chosen for study were representative of typical facilities, both new and old. However, the study does require more testing of the older, oil-burning asphalt plants.

The concept for the project was formulated after attempts to estimate PAH emissions from asphalt plants for enforcement purposes were largely unsuccessful. Previously, estimated emissions of PAH or polycyclic organic matter (POM) from asphalt plants were based on limited non-specified test data<sup>1</sup>. In addition, CT's existing hazardous air pollutant regulation for PAH was unclear and difficult to enforce because it was defined as PAH (benzene soluble). As an interim policy designed to facilitate the permitting of new asphalt plants, provisions were included in new permits to require testing for PAHs consequent to the development of an appropriate test method. As a result of this study, CT DEP now regulates specific PAH compounds and can specify a particular test method.

## EXPERIMENTAL METHODS

### Sample Collection

Two of the facilities CT DEP tested were at the Balf Company of Newington, which operates both batch and express or drum mix asphalt plants. The batch plant has a maximum operating capacity of 10 tons/batch while burning natural gas. The asphalt express process is a Gencor-Bituma drum mix asphalt plant. This plant has a maximum operating capacity of 450 tons/hour while burning natural gas. Both operations utilize a baghouse for particulate removal.

The PAH/NHC emissions from the plants were sampled in triplicate according to SW 846 Method 0010. The volumetric flowrate, moisture content, and stack gas composition were determined during each test run. All testing was performed on the exhaust stack. In conjunction with PAH/NHC testing, EPA Methods 1 through 4 were performed.

The PAH/NHC sampling method used the modified Method 5 sampling train. A modification in the sample recovery procedure was used and consisted of replacing the 1:1 mixture of methanol/methylene chloride rinse with separate rinses of acetone and methylene chloride. An acetone rinse followed by a methylene chloride rinse has been shown to be more efficient than the methanol/methylene chloride (1:1 volume) rinse. The PAH/NHC sampling method also included several unique preparation steps which ensured that the sampling train components were not contaminated with organics that may have interfered with analyses.

Triangle Laboratories, Inc. (TLI), Research Triangle Park, North Carolina performed the preparation of the glass fiber filters and the XAD-2 resin. All filters were cleaned before their initial use. The methylene chloride extract from the filter cleaning procedures was analyzed for PAH/NHCs. If any PAH/NHC was present in the concentration above the minimum detectable limit, the cleaning procedure was repeated and the extract reanalyzed until no PAH/NHC was detected.

The XAD-2 resin was placed in a soxhlet and extracted with HPLC grade water, methanol, and methylene chloride. After extraction, the resin was dried and placed in the sampling cartridges which were tightly capped with glass plugs. The extracts were then analyzed for total chromatographic organics (TCO) and targeted PAH/NHC compounds. If any PAH/NHC were present at a concentration above the minimum detectable limit and/or the TCO was greater than 20 ug/ml, the cleaning procedure was repeated until each criteria was met. In addition, the resin of each trap was fortified with 100 pg/ml of d14-Terphenyl<sup>2</sup>.

### Sample Analysis

High resolution gas chromatography/high resolution mass spectroscopy (HRGC/HRMS) analytical methodology was developed by TLI to satisfy CT DEP's monitoring objectives<sup>3</sup>. These objectives included determining the analytical feasibility of monitoring for 29 polynuclear aromatic hydrocarbons and five nitrogen heterocycles in asphalt plant stack samples. These compounds are listed in Table 1.

Table 1.  
List of Target Polycyclic Aromatic Hydrocarbons  
and Nitrogen Heterocycles.

Naphthalene	2-Methylnaphthalene	Acenaphthene
2-Chloronaphthalene	Acenaphthalene	Fluorene
Phenanthrene	Anthracene	Carbazole
Acridine	Fluoranthene	Pyrene
3-Methyl-fluoranthene	Cyclopenta-c,d-pyrene	Benzo-a-anthracene
Chrysene	Perylene	Benzo-b-fluoranthene
Benzo-j-fluoranthene	Benzo-k-fluoranthene	Benzo-a-pyrene
Benzo-e-pyrene	7H-Dibenzo-c,g-carbazole	Benzo-[ghi]-perylene
Dibenz-[ah]-anthracene	Dibenz-[aj]-anthracene	Dibenz-[aj]acridine
Dibenz-[ac]-anthracene	Dibenz-[ah]-pyrene	Dibenz-[ai]-pyrene
Dibenz-[ae]-pyrene	Dibenz-[al]-pyrene	Indeno-[1,2,3-cd]-pyrene
7,9-Di-Methyl-benz-c-acridine		

No problems were noted by TLI's sample preparation and mass spectrometry groups while performing the analyses. However, several factors did impact data validity. One of the factors was matrix related interferences which affected the quantitation of some analytes. This problem was described as severe in some samples. Quantitation of naphthalene, chloronaphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, acridine and carbazole could not be performed in a particular sample as a result of the matrix interference. TLI did provide quantitative results for these analytes in that sample which were believed to be minimum estimates. However, these values were not reliable enough to support an enforcement action. High recoveries of some internal standards were calculated in samples as a result of this interference. TLI modified their cleanup procedures in an attempt to more effectively remove the matrix interferences.

A second factor was that the results of all samples displayed selective losses during extraction for the labeled acridine and carbazole internal standards. Since the associated analytes act chemically in the same fashion, it can be assumed that these and other nitrogen heterocycles are selectively lost during extraction.

Another factor was that "b" and "j" isomers of benzofluoranthene as well as the "ac" and "ah" isomers of dibenzoanthracene coelute. Therefore, quantitative results were provided as a total for each isomer pair.

The last factor of concern was that saturated peaks (i.e. beyond calibration) were noted in all the samples. TLI believed that quantitative results for saturated signals were "minimum estimates".

The total PAH concentration was calculated for each sample. Naphthalene, 2-methylnaphthalene, and 3-methylfluoranthene were not included in the total PAH concentrations.

## RESULTS

CT DEP reviewed data from both oil and natural gas-fired batch operations as well as batch and express plant operations. Table 2 lists the comparison of data from asphalt batch and express processing plants firing natural gas. Table 3 shows a comparison of three asphalt batch plants. The Balf and Astec plants were firing natural gas. The Tilcon plant was firing No. 2 oil.

Table 2.  
Natural Gas-Fired Asphalt Batch and Express Plants  
PAH Data Excluding Naphthalene (ug/m<sup>3</sup>).

<u>Analyte</u>	<u>BATCH</u>	<u>EXPRESS</u>
Acenaphthene	1.75 (27%)	0.364 (9.4%)
Acenaphthylene	0.25 (4%)	1.185 (31%)
Fluorene	2.28 (36%)	0.848 (22%)
Phenanthrene	1.88 (29%)	1.147 (30%)
Anthracene	0.06 (1%)	0.066 (1.7%)
Fluoranthene	0.05 (1%)	0.119 (3.1%)
Pyrene	0.07 (1%)	0.081 (2.1%)
Benzo-a-Anthracene	6.7E-4 (.01%)	0.003 (.08%)
Chrysene	0.01 (0.2%)	0.024 (0.6%)
Benzo-k-Fluoranthene	0 (0%)	0.002 (.04%)
Benzo-j-Fluoranthene	0 (0%)	0 (0%)
Benzo-b-Fluoranthene	0.0017 (.03%)	0.005 (.12%)
Benzo-e-Pyrene	0.005 (.08%)	0.008 (.21%)
Benzo-a-Pyrene	0.0007 (.01%)	0.003 (.08%)
Indeno-123-cd-Pyrene	0.0027 (.04%)	0.003 (.08%)
Benzo-ghi-Perylene	0.027 (.43%)	0.023 (0.6%)
Dibenzo-ah-Anthracene	0 (0%)	0 (0%)
<u>Total PAH</u>	<u>6.4</u>	<u>3.9</u>

## DISCUSSION

The majority of the observed PAH emissions were comprised of: acenaphthene (24%), acenaphthylene (10.7%), fluorene (34.3%), phenanthrene (22.6%), anthracene (2.7%), fluoranthene (2.4%), and pyrene (1.8%). These 7 PAHs make up approximately 98-99% of the PAHs identified in the stack effluent samples. Naphthalene, 2-methylnaphthalene, and 3-methylfluoranthene were not included.

Emissions from the No.2 fuel oil fired batch process appeared to be twice the emissions from the natural gas fired process. Emissions from the express drum mix plant appear to be 40% lower than the batch plant (both plants natural gas-fired). Although the data base was quite small, it appeared that acenaphthylene was significantly more prevalent in the express plant samples. Correspondingly, acenaphthene seemed to be far more predominant in the batch samples.

## CONCLUSIONS

### Regulatory Implications

The following analytes were dropped from the target list of PAH/NHC compounds: 2-chloronaphthalene, carbazole, acridine, cyclopenta-cd-pyrene, dibenz-aj-acridine, 7,9-dimethyl-benz-c-acridine, perylene, 7H-dibenzo-cg-carbazole, the "ac" and "aj" isomers of dibenzanthracene, and the "ai", "ae", "ai", and "ah" isomers of dibenzpyrene. These compounds were seldom if at all detected and then, only at trace levels in samples which contained relatively high PAH levels (especially when compared to ambient concentrations).

Table 3

Asphalt Batch Plants PAH Data Excluding Naphthalene (ug/m3).

<u>Analyte</u>	<u>BALF</u>		<u>ASTECC</u>		<u>TILCON</u>	
	Natural Gas-Fired 10 ton/batch		Natural Gas-Fired 4 ton/batch		No. 2 Oil-Fired 5 ton/batch	
Acenaphthene	1.75	(27%)	1.46	(22.5%)	3.12	(28%)
Acenaphthylene	0.25	(4%)	1.19	(18.3%)	0.37	(3.3%)
Fluorene	2.28	(36%)	1.26	(19.4%)	5.18	(47%)
Phenanthrene	1.88	(29%)	2.2	(33.8%)	1.09	(9.8%)
Anthracene	0.06	(1%)	0.032	(.5%)	0.6	(5.4%)
Fluoranthene	0.05	(1%)	0.133	(2%)	0.36	(3.2%)
Pyrene	0.07	(1%)	0.117	(1.8%)	0.23	(2.1%)
Benzo-a-Anthracene	6.7E-4	(.01%)	0.004	(.06%)	0.016	(0.14%)
Chrysene	0.01	(0.2%)	0.015	(.23%)	0.086	(0.77%)
Benzo-k-Fluoranthene	0	(0%)	0.003	(.05%)	6.7E-4	(.006%)
Benzo-j-Fluoranthene	0	(0%)	-		0	(0%)
Benzo-b-Fluoranthene	0.0017	(.03%)	0.013	(0.2%)	0.006	(0.05%)
Benzo-e-Pyrene	0.005	(.08%)	0.006	(.09%)	0.008	(0.07%)
Benzo-a-Pyrene	0.0007	(.01%)	0.0019	(.03%)	6.7E-4	(.006%)
Indeno-123-cd-pyrene	0.0027	(.04%)	0.003	(.05%)	0.006	(0.05%)
Benzo-ghi-Perylene	0.027	(.43%)	0.058	(0.9%)	0.044	(0.4%)
Dibenzo-ah-Anthracene	0	(0%)	0.0014	(.02%)	0	(0%)
<u>Total PAH</u>	<u>6.4</u>		<u>6.5</u>		<u>11.1</u>	

CT DEP now requires SW846 0010 as the PAH test method. Acetone and methylene chloride are to be used as the sample recovery solvents. Analysis is performed with HRGC/HRMS. Monitoring for nitrogen heterocycles requires additional method development and validation as well as separate sampling and analyses from PAHs. Therefore, CT DEP is not requiring sources to test for NHCs.

The asphalt plants fired with natural gas were generally well below CT DEP's maximum allowable stack concentration for PAH. The plant fired with No. 2 fuel oil was approximately 5 times the allowable stack concentration.

CT DEP has developed a proposed regulation for PAH and naphthalene as a result of this project. The ambiguity of the existing definition and multiple listings of PAH compounds in the regulations hampered both the CT DEP and the sources in determining compliance and performing appropriate monitoring.

CT DEP proposed the following definition be added to the regulations: (PAH) will be defined as the sum of the following compounds: acenaphthene, acenaphthylene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(k)fluoranthene, benzo(j)fluoranthene, benzo(b)fluoranthene, benzo(e)pyrene, benzo(a)pyrene, indeno-1,2,3-cd-pyrene, benzo-ghi-perylene, dibenzo-ah-anthracene.

CT DEP proposed the following items be deleted from the existing regulations: benz(a)pyrene, coal tar pitch volatiles, polynuclear aromatic hydrocarbons (PAH), benz(a)anthracene, benzo(b)fluoranthene, chrysene, 7H-dibenzo(c,g)carbazole, dibenzo(a,h)anthracene, dibenzo(a,h)pyrene, dibenzo(a,i)pyrene, indeno(1,2,3-cd)pyrene, and, asphalt (petroleum) fumes. CT DEP also proposed to redefine "naphthalene" as the sum of both naphthalene and 2-methylnaphthalene.

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*Session 11*

*Measurement of Aerosols*

**The Summer 1992 PM-10 Saturation Monitoring Study  
in the Ashland, KY Area**

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A PM-10 saturation monitoring field study was conducted in the Ashland, Kentucky area during July and August, 1992. The study was sponsored by The U.S. Environmental Protection Agency (EPA), Office of Air Quality Planning and Standards, in cooperation with EPA Region IV. The study area extended across State and Regional borders into Ohio (Region V) and West Virginia (Region III). The purpose of the study was to evaluate the use of portable PM-10 monitors in examining the potential for exceedances of the NAAQS in the area and to make recommendations for optimizing permanent monitoring locations. This paper presents the results of the study and highlights issues of interest for the successful utilization of PM-10 saturation monitoring in PM-10 ambient monitoring network reviews.

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## INTRODUCTION

A PM-10 saturation monitoring field study was conducted in the Ashland, Kentucky area during July and August, 1992. The study was sponsored by the U.S. Environmental Protection Agency (EPA), Office of Air Quality Planning and Standards, Technical Support Division, in cooperation with EPA Region IV. The impact area extends across State and Regional borders into Ohio (Region V) and West Virginia (Region III). These States and Regions provided input for the study design and assistance in the study implementation. The purpose of the study was to evaluate the use of portable PM-10 monitors in examining the potential for exceedances of the NAAQS in the area, and to make recommendations for optimizing permanent monitoring locations. The portable monitors are not USEPA reference/equivalent methods, and the data collected cannot be used to support regulatory or enforcement actions. The primary monitoring objective was to identify high concentration areas. A secondary objective was to characterize the overall spatial distribution of PM-10 concentrations in the area.

## STUDY DESIGN AND IMPLEMENTATION

### Network Design

The network provided spatial coverage of the industrialized area centered at the confluence of the Ohio and Big Sandy Rivers. The network was focused on the industrial sources of PM-10 in the area. This included a steel mill, a coke plant, an ethanol plant, an oil refinery, a chemical plant, and a carbon reclamation plant. Several large coal tipples were also considered in selecting site locations. Each major source was covered with upwind and downwind monitors relative to seasonal predominant winds from the southwest. Upwind monitors recorded background conditions including emissions from area sources (especially unpaved roads) and more distant point sources.

The network included both elevated (hilltop) and base level sites to cover impacts from stack and ground-level fugitive emissions. Sites were selected to represent potential PM-10 impacts from both point and fugitive sources near the site. Existing monitoring data, emissions information, meteorology and topographical influences were all considered in the network design. In addition, citizen complaint records were used to identify potential high impact areas. Site locations avoided influences from immediate local sources such as unpaved roads, railroads, or agricultural activity. Twenty three portable monitors were available for the study. This allowed for establishing 19 sites, given that 2 monitors were reserved as spares and 2 sites were collocated. With this number of sites, it was possible to locate sites in expected high concentration areas near sources and distribute the sites reasonably uniformly over the study area. Figure 1 shows a map of the study area.

Meteorological data were collected during the study from the national weather service station located at Huntington Airport (Huntington, WV), the Cooper School (Catlettsburg, KY) meteorological station operated by the Kentucky Division for Air Quality, and a special station set up for this study at Riverview Nursing Home (Russell, KY). The Huntington Airport station is located in West Virginia at the eastern end of the study area. The Cooper School station is located on a hilltop on the Kentucky side of the Big Sandy River, and is collocated with site #15. The Riverview station was located along the Ohio River at the north end of the study area, and collocated with site #04.

### Description of Portable Samplers

The portable PM-10 saturation samplers used in the study were designed and built by the Lane Regional Air Pollution Authority (Springfield, Oregon). The samplers are battery operated and are typically mounted on a utility pole. The inlet is designed to achieve the PM-10 particle size cut point at a flow rate of 5 actual liters per minute (lpm). The flow rate for each sampler is calibrated at the laboratory and checked periodically during operation. Flows are read from a rotameter at the start and end of each sampling period. Constant flow is maintained by circuitry that adjusts the pump speed in response to normal variations due, for example, to filter loading during the exposure interval. The sampler will automatically shut down if it is unable to maintain flow within a specified interval. This could occur due to an obstruction in the flow lines, excessive filter loading, or if the battery is unable to provide sufficient voltage to maintain the proper pump speed. The normal exposure interval is 24 hours. The sampler is provided with a programmable timer and an elapsed time meter to record the exposure interval.

### Sampling and Analysis

Sampling was conducted from July 11 through August 18, 1992. This period was selected based on the months when the highest particulate concentrations have historically been recorded in the area. Sampling was conducted on a daily basis at all 19 sites. Two of the sites were collocated, so a total of 21 filters were exposed each day. Samples were changed between 4pm and 8pm each day, with the goal of completing sample changes between 4pm and 6pm. The network was spread over a relatively large area and travel was restricted by bridge locations across the two rivers. Two

operators were required to complete the sample changes within a 2 to 4 hour time window. Local operators were recruited and trained for routine daily operations and quality control checks. Each sample was exposed for approximately 24-hours. Actual start and end times were staggered according to the time required for the operator to reach and service the sites. Samples were shipped weekly to the laboratory for weighing.

#### Filter Media

Both quartz fiber and Teflon filters were used in the study. Many previous PM-10 saturation studies have used quartz fiber filters. These filters are inexpensive and are well suited for gravimetric analysis; however, they are not well suited for microscopy or elemental analysis. Several of the study participants were interested in archiving filters from this study for future microscopy and/or elemental analysis. Therefore, Teflon filters were obtained for use at three selected sites to provide a higher quality media for future analysis. The sites were selected in areas where impacts from multiple sources might be expected (sites #05, #09, and #13) since the results from microscopic and/or elemental can be used to identify source types and relative source contributions.

The quartz filters are extremely friable, and are easily damaged during sample handling, storage, and shipment. Early reports from the laboratory indicated that 25 to 30 percent of the quartz filters collected during the first two weeks of the study were damaged during sample handling. The damage occurred because the filter holder compressed the edge of the filters. The edges would then partially separate during cold storage and shipment. The filters were intact when removed from the filter holders by the operators. Detecting the problem was delayed because the damage was only evident after the filters were inspected at the laboratory. The problem was corrected by instructing the operators to tighten the filter holders no more than necessary. Cold storage of the filters was also eliminated as an added precaution. These corrective actions were implemented on July 24. After that date, far fewer filters were damaged. Starting August 12, Teflon filters were used at all sites. No filter damage occurred when using Teflon filters. The low pressure drop type of Teflon filters that were used caused no noticeable decrease in sampler flow rate compared to using quartz filters.

#### DATA QUALITY AND SAMPLER PERFORMANCE

A rigorous quality assurance and quality control program was implemented for the study. This program was designed to assure that the study produced data of known quality and to provide information that could be used to evaluate the performance of the portable monitors. An assessment of data quality and comparability with USEPA reference/equivalent methods was a key component of the study. In addition to provisions for proper sampling and analytical procedures, the quality assurance plan provided for collocated sampling, duplicate weighings, collection of field blanks, and internal and external flow audits. All data were carefully validated before analysis based on laboratory observations, filed logs, and operator contacts.

Duplicate portable monitors were located at two sites (#12 and #05). Site #12 also contained a single PM-10 reference monitor operating on a 1 in 6 day sampling schedule. Site #05 contained two reference PM-10 monitors that were operated twice each week on a 5 pm to 5 pm sampling schedule and a continuous PM-10 monitor (TEOM). Overall precision based on the collocated sample pairs was about 15% (quartz) and 5% (Teflon). A comparison of data from the collocated portable and reference monitors (including the TEOM) was used to assess the performance of the portable monitors relative to EPA reference/equivalent methods. On average, the portable monitors gave results about 5  $\mu\text{g}/\text{m}^3$  higher than the reference PM10 monitors and about 10  $\mu\text{g}/\text{m}^3$  higher than the TEOM.

Two laboratories were involved in the study; the Lane Regional Air Pollution Authority (LRAPA) laboratory and the South Carolina Department of Health and Environmental Control (SC-DHEC) laboratory. Primary analyses were conducted by the LRAPA laboratory. The LRAPA laboratory also provided the pre-weighed filters. The SC-DHEC laboratory performed duplicate weighings (tare and exposed) on about 8 percent of the filters. The difference between the two weighings amounted to no more than about 1 to 2  $\mu\text{g}/\text{m}^3$  at a typical exposure volume (7.5  $\text{m}^3$ ).

Each operator exposed approximately 2 field blanks per week for a total of 24 blanks (15 quartz and 9 Teflon) for the study. The blanks were exposed by loading a filter into a spare sampler and mounting the sampler alongside an operational sampler during a normal sampling interval. Blank filters were logged, handled, shipped and analyzed according to standard operating procedures. The field blanks were used to provide information on the effects of sample handling, storage, and shipping on PM-10 concentrations. A detection limit taken as the sum of the average blank result and twice the standard deviation of the blank results is about 12  $\mu\text{g}/\text{m}^3$  for both quartz and Teflon filters.

A multipoint flow calibration (6 points) was conducted on each sampler at the LRAPA lab before the samplers were shipped to Ashland. The standards used at the LRAPA laboratory are traceable to NIST volume standards. The

set point was established to achieve an actual flow of 5 lpm based on the summer seasonal average temperature and pressure for the study area (293.1 °K, 739.9 mm Hg). During sampler set-up and check out, the flow rate on each sampler was checked with a bubble flowmeter (0-30 actual lpm). An independent flow rate check was performed on 17 of the 23 samplers by the State of Kentucky on August 5. All samplers audited were within about  $\pm 10$  percent of 5 lpm. Flow rates were again checked against a standard at the end of the study before they were removed from the area. All samplers were within  $\pm 10$  percent of 5 lpm.

A total of 787 PM-10 samples were collected during the study (570 quartz, 217 Teflon). Overall, 81 percent (639) of the samples collected were valid; however, 90 percent (196) of the Teflon samples were valid, while only 78% (443) of the quartz filters were valid. The study goal was to obtain 30 valid samples from each site. This was very nearly accomplished except at site #10, where sampling was discontinued mid-study so that the sampler could be used to replace a sampler stolen from site #13.

Sufficient valid data were obtained to satisfy the study objectives. Data quality improved significantly after the problem with damaged filters was successfully corrected. Further data quality improvements were realized with the Teflon filters. The samplers performed adequately for the purpose of identifying high concentration areas where there may be a potential to exceed the NAAQS. With careful sample handling, adequate performance can be attained using either quartz or Teflon filter media; however, Teflon filters gave better results for all data quality indicators and were easier for the operators to handle.

#### DATA SUMMARY AND ANALYSIS

The concentration data were symmetrically distributed with a mean of  $37 \mu\text{g}/\text{m}^3$  and a median of  $36 \mu\text{g}/\text{m}^3$ . The maximum value was  $135 \mu\text{g}/\text{m}^3$ . This value was recorded at site #01 on July 15. This is an exceptionally high value, given the overall distribution of the data. The second highest value was  $82 \mu\text{g}/\text{m}^3$ , and was recorded at the same site on July 9, 1992.

Figure 2 summarizes the PM-10 levels recorded for each site and date using grouped boxplots. The horizontal line across each box represents the median of the data. The central 50 percent of the data are represented within each box. The vertical lines on each end of the box (whiskers) extend to the last data point within 1.5 times the height of the box on either side of the median. For normal distributions, the whiskers encompass about 95 percent of the data. Data lying outside the whiskers represent exceptionally high values. Such points are plotted as circles or pluses. The pluses ("+" ) represent points that fall outside of an upper limit of twice the box height above the median. The width of each box is proportional to the square root of the number of points represented. The width of the notches in the sides of the boxes approximates a 95 percent confidence interval about the median. Two sites or dates can be compared by comparing the notches. If the notches do not overlap, the median concentrations are different at a 95 percent confidence level.

All sites are represented by a comparable number of samples (28 to 37), except for site #10 which is represented by only 14 measurements. The majority of the PM-10 measurements across the study area fall within approximately the same range (about 30 to  $50 \mu\text{g}/\text{m}^3$ ); however, PM-10 levels at sites #1, #7 and #18 tend toward the higher values. The high value recorded at site #01 is omitted from Figure 3 for clarity. Each date may be represented by up to 21 valid samples; however, most days are represented by about 15 to 20 valid samples. A curve is fitted (cubic spline fit) through the daily data to represent the general trend of PM-10 levels over time. Peaks in this curve could be associated with upsets or with meteorological conditions conducive to high concentration levels.

#### NETWORK REVIEW AND CONCLUSIONS

The study was scheduled to coincide with the time of year when maximum PM-10 concentrations have historically been measured in the area. Before the existing network's ability to capture maximum PM-10 concentrations in the area can be evaluated, it should be established that the meteorological and emissions conditions prevailing during the summer of 1992 are representative of those prevailing in previous years. It should also be considered whether such conditions are likely to prevail in future years. Such comparisons can be addressed in terms of changes in PM-10 source emissions, changes in meteorological conditions, and by comparison of study results with ambient monitoring data from previous years.

Little information was obtained for the study on the emission rates, in recent years, for the various point sources in the area. Historical data through 1988 were obtained from the report titled *Air Pollution Study of Ashland, Kentucky* -

*Huntington, West Virginia - Ironton, Ohio Tri-State Area.*<sup>1</sup> In general, emission controls implemented at the various facilities throughout the 1980's have resulted in improved air quality in the area; however, upsets can still have a significant impact. No upsets were reported during the study period. The steel mill was in the process of installing new control equipment during the study period, and emissions from the existing equipment may have been greater than normal. Immediately following the study, however, operations at the steel plant were greatly reduced for economic reasons. With the new control equipment in place, and the reduced scale of operations, emissions from this facility should be much lower in future years.

The weather during the summer of 1992 was unusually cool and fair in the Ashland area, as it was over much of the United States. The Ashland Regional Office of the Kentucky Division for Air Quality reports that there were no truly poor air quality days during the study period. Based on previous years, at least several poor air quality days associated with strong inversions and air stagnation should be expected during July and August. The summertime median and maximum PM-10 levels obtained at existing sites in the area were reviewed since the initiation of PM-10 monitoring in the area (1986 through 1991). The median and maximum concentrations over this period are consistent with those obtained for the saturation study. That is, the 1992 saturation study results are representative of the historical monitoring record for the area.

The Ashland area has historically been subject to relatively intense monitoring activity due to the concentration of industry and the tendency for strong summertime inversions that concentrate pollutants in the area. The existing PM-10 monitoring stations span the saturation study area and provide reasonable spatial coverage, but are not as densely spaced as the saturation network. The existing sites tend to be population exposure oriented, while the saturation study sites were chosen to represent expected maximum concentration areas. In particular, the areas represented by the saturation study sites reporting the highest overall concentrations are not well represented by the existing network. These saturation study sites include site #01 (Ironton, Ohio) site #07 (Ashland, KY) and site #18 (Wayne County, WV).

Site #01 is located nearer to point sources of PM-10 than the existing sites in Coal Grove and Ironton, Ohio, and appears to capture higher PM-10 concentrations than those sites. Site #01 may not be as representative of population exposure as the sites in Coal Grove and Ironton since it is not located in a primarily residential area, but it may represent a maximum concentration site for the area. PM-10 monitoring was recently initiated (August 1992) in the area near site #07. The area around site #18 is not densely populated; however, this location may serve as a maximum concentration site.

No valid PM-10 measurements exceeding the 24-hour PM-10 standard of 150  $\mu\text{g}/\text{m}^3$  were recorded during the study period. Most concentrations were well below the standard. PM-10 levels were fairly uniform across the area represented by the network and generally fell within the range from 30 to 50  $\mu\text{g}/\text{m}^3$ . Because no exceedances of the level of the PM-10 NAAQS were recorded during the saturation study, and few values approaching the PM-10 standard were measured, no changes to the existing PM-10 monitoring network in the area were recommended. However, establishing additional maximum concentration oriented sites in the areas represented by saturation site #01 and #18 would improve the ability of the existing network to capture the highest PM-10 levels that occur.

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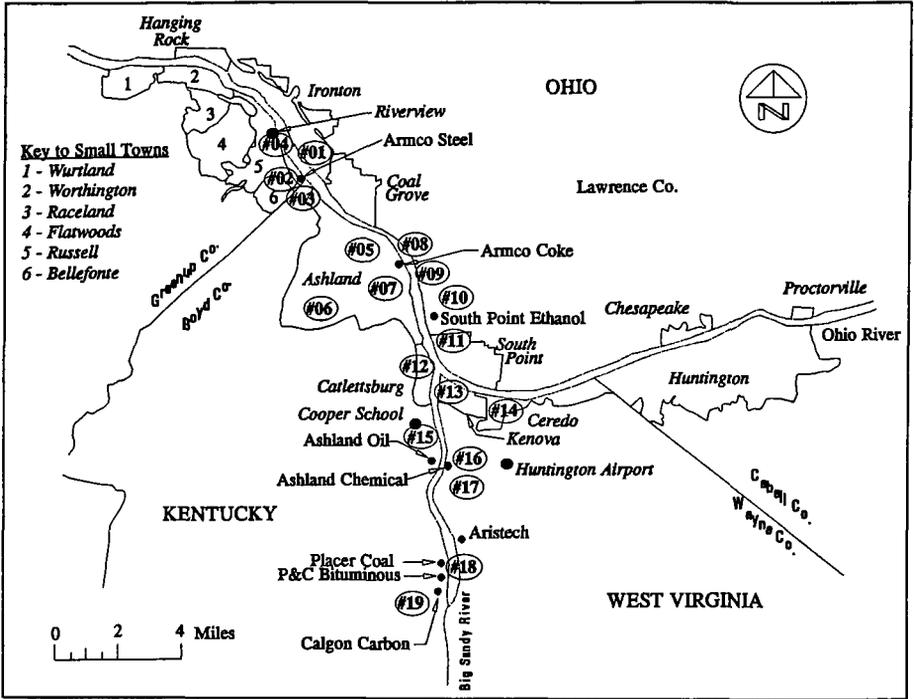


Figure 1. Map of the Study Area

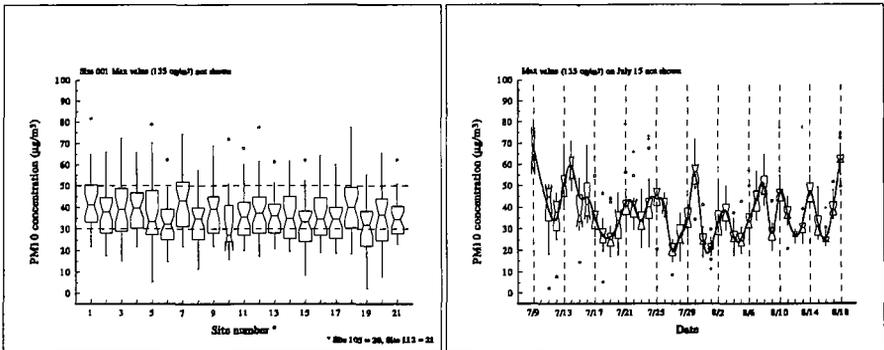


Figure 2. PM-10 Concentration Summary by Site and Date

# Evaluation of a Real-Time Monitor for Particle-Bound PAH in Air

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## ABSTRACT

An instrument for semi-quantitative real-time measurement of polycyclic aromatic hydrocarbons (PAH) on airborne fine particles was evaluated. The instrument operates on the principle of photoelectric ionization of PAH adsorbed on particle surfaces, with resulting loss of photoelectrons and subsequent measurement of the remaining positively charged particles. We investigated the characteristic performance of the instrument in both chamber and field studies. This performance included: selectivity for fine particles, response to PAH only on particles versus response to PAH in the vapor phase, accuracy compared to integrated sampling, interferences, rapidity of response, limits of detection, bias, ease of operation, reproducibility, calibration, reliability, and ease of field operation and maintenance. The instrument performed well and appears to be suitable for screening air for particle-bound PAH in a variety of microenvironments, as well as for use in estimating human exposure related to various activities that may generate PAH.

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. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

## INTRODUCTION

A newly developed monitoring instrument intended for real-time measurement of PAH on airborne fine particles, the PAS 1000i (EcoChem Technologies, Inc., West Hills, California), was evaluated in our laboratories for its potential use in ambient and indoor air measurements and in human exposure research. To accomplish this evaluation, we obtained two monitors and carried out a variety of experiments with them in the laboratory and in several microenvironments.

### Principle of Operation

The PAH monitor operates by photoelectric ionization of PAH adsorbed on the surface of carbon aerosols.<sup>1-5</sup> Air is drawn into the instrument by an internal pump at a flow rate of 4 L/min and passes through an electrostatic precipitator to remove ionized particles or charged gas molecules. Light at a wavelength of 185 nm from an ultraviolet lamp then selectively ionizes the PAH on the surface of the particles, while the gases and

other aerosols remain neutral. Diffusion or acceleration by an applied electric field removes the photoemitted electrons and the gases from the airstream. The remaining positively charged particles are collected on a filter inside an aerosol electrometer, where the charge is measured. The electrometer current is proportional to the total concentration of photoionizable particles in the air stream and hence proportional to the particle-bound PAH concentration.

Because of the lower photoelectric threshold for larger PAH, which results from their large  $\pi$ -electron systems, photoionization is most effective for PAH with four or more rings. Additionally, because of the smaller likelihood of recapture of photoemitted electrons, photoionization is most effective for PAH < 1-2  $\mu\text{m}$  diameter. This effectiveness is enhanced for PAH on carbonaceous (typically combustion-generated) particles and for PAH with planar molecular structures and packing. For example, it is more effective for benzo[a]pyrene, which is planar, than for rubrene, which is non-planar.<sup>5</sup> For a given type of combustion, such as heating with fuel oil or automotive gasoline combustion, the PAH profile is relatively constant.<sup>6</sup> This allows an approximate universal calibration of the monitor current with PAH concentration to be inferred. A large variety of experiments indicates that the universal calibration is independent of the type of aerosol within a factor of two.<sup>7</sup> Good correlations of the photoemission with individual PAH concentrations ( $r=0.95$  for phenanthrene and  $r=0.97$  for fluoranthene spiked on carbon particles;  $r=0.94$  for benzo[a]pyrene in cigarette smoke) measured by conventional means — extraction and gas or thin-layer chromatography — have also been demonstrated.<sup>8,9</sup> The photoelectric signal is the sum of the signals from the individual surface-adsorbed PAH.<sup>10</sup>

To date, the greatest number of applications of photoelectric charging to PAH measurement have been in the laboratory, and most of the applications have been to emissions characterization. For example, a study of PAH aerosols in oil stove emissions and automobile exhaust demonstrated a strong correlation between the photoemission and the total PAH.<sup>11</sup> A few investigations studied PAH aerosols in ambient air. For example, in downtown Zürich and in Hannover, the signals from the monitor followed the diurnal patterns and total particle counts in the ambient air; additionally the lower response of the instrument to aged ambient aerosols demonstrated its greater sensitivity to fine particles.<sup>12</sup>

## EXPERIMENTS AND RESULTS

### Instrument characteristics

Two monitors were operated continuously for periods of 8 hr to 1 mo in our laboratory. They were collocated and positioned variously: on top of one another, immediately beside each other, about 5 ft apart at opposite ends of a bench, and in the middle and near the walls of the room. Stability was excellent; no anomalous results were observed; set-up was simple; and no repair or re-zeroing of the instruments was necessary. Excellent agreement between the results from the two instruments was obtained; a typical correlation factor between the 1-min average concentrations from the two units was  $r^2=0.999$  (in this case, for a 48-hr experiment).

To confirm that the monitor responds only to particles, the instruments were challenged in the laboratory with many different chemical vapors, including naphthalene, indene, anthracene, and other aromatic vapors. They gave no response, as expected. Additionally, no response to 200-500 ppb of the PAH indene in the vapor phase was observed in a chamber in which the particle count was 1-3/cm<sup>3</sup>.

The physical principles of the PAH monitor should make it more sensitive to PAH on fine particles. To confirm this fine-particle selectivity, we ran two instruments, one

with and one without a 2.5  $\mu\text{m}$  size-selective inlet,<sup>13</sup> for periods of 1-3 days, side by side in a laboratory served by ca. 50% outside air from vents near the building parking area. The monitors clearly followed PAH-generating events, including heavy traffic in the parking area and activity of utility vehicles. No difference was observed between the responses of the two units.

The sensitivity of the monitor, if one uses the manufacturer's calibration factors, is 1 pA per 1000-3000 ng/m<sup>3</sup>. We observed a limit of detection of about 10 ng/m<sup>3</sup>.

Because the irradiation from the ultraviolet lamp must be of sufficient energy to overcome the photoelectric ionization threshold of the PAH and to remove the photoelectrons from the surface of the particles, a slightly more energetic radiation (185 nm (6.7 eV) is used, compared to the optimum photoabsorption for PAH, which is nearer to the 254 nm used in some of the early work. Interference is expected from some metals and organics. However, photoemission from inorganics such as sodium chloride should not occur (higher energy is required; for example, the work function for sodium chloride is 8.57 eV). Literature reports indicate that photoemission from sodium chloride particles does not occur when the salt is coated with aliphatic hydrocarbons, nor does it occur in the absence of adsorbate.<sup>14</sup>

However, in our chamber experiments, the monitors responded to sodium chloride aerosols in three size ranges [0.04, 0.08, and 0.15  $\mu\text{m}$  concentration mean diameter (CMD), 22,500-50,000 particles/cm<sup>3</sup>]. This response was variable and small, compared to that for typical indoor PAH concentrations. For example, the monitor gave a response of 0.175 pA to 50,000 NaCl particles/cm<sup>3</sup> at the largest CMD above, but for similar concentrations of environmental tobacco smoke (ETS), with 0.05-0.4  $\mu\text{m}$  particles, the response was 2.5 pA, more than an order of magnitude higher. Analysis of the bulk salt indicated trace amounts of phthalates, suggesting that the adsorbed impurities on the salt aerosol were responsible. Burtscher<sup>15</sup> repeated our work, and he too found a response to supposedly pure sodium chloride. Heating the salt to 800 C before formation of the aerosol reduced the response to <8 fA and thus confirmed the role of impurities. It is expected, therefore, that the instrument may normally exhibit a small positive bias due to non-PAH impurities.

Little effect of temperature was observed on the monitor response, except that attributable to changes in the distribution of PAH between vapor and particles as a result of changes in their vapor pressures with temperature. Possible quenching of photoemission by high water concentrations has been suggested.<sup>8</sup> We are investigating this possible influence of high humidity.

The electrostatic precipitator (ESP) in the initial section of the instrument is intended to ensure that the incoming aerosol is electrically neutral. However, operation of the monitor with and without the ESP made no difference in the results. The ESP may be needed in the emissions version of the monitor, where particles may initially be far from charge equilibrium. However, the ESP appears to serve little useful function for indoor or ambient air aerosols, which are normally at charge equilibrium, and may in fact cause some particle losses.

Calibration of the instrument is done by the manufacturer, and is limited to calibration of the ionizing unit based on its ozone production.<sup>7</sup> In field experiments, we used a butane lighter, a kitchen match, or a cigarette to estimate the calibration and test the response of the instrument. The monitor response agreed with that from collocated integrated sampling within a factor of 1 to 4, using a calibration factor of 3000 ng/m<sup>3</sup>-V. High concentrations of fine-particle PAH required a lower calibration factor; for example ETS, which is rich in fine particles, required a calibration factor of 1000 ng/m<sup>3</sup>-V to produce agreement with the results of integrated sampling. For higher quantitative accuracy, source-specific calibration is desirable.

### **Instrument field operation**

To evaluate the performance of the PAH monitor in field situations, we incorporated it in several small studies and used it in a variety of environments. These included long-term evaluation in the laboratory, which we discussed previously; shipment, field set-up, and operation in a study of indoor air in some newly constructed homes in Colorado; monitoring fireplace operation and other combustion activities in two EPA employees' homes; monitoring smoking, traffic patterns, and other activities inside and outside a veterinarian's office near a busy highway; monitoring fine-particle air exchange in a house with an attached garage; monitoring smoking and other combustion activities in shops, bars, and restaurants; and monitoring PAH concentrations in homes with collocated integrated sampling. Throughout the experiments, the monitors performed well, survived shipment with no problems, were easy to set up and run, and followed external combustion events precisely. There was no significant down-time.

The results of monitoring outside a home in a neighborhood heavily impacted by wood smoke are shown in Figure 1. Over the weekend, many homeowners used their fireplaces, which produced high concentrations of respirable suspended particulate material (RSP), as measured with a piezobalance, and high concentrations of fine-particle PAH. Then at the beginning of the workweek, the fireplace use diminished, but automotive traffic increased substantially, leading to increased PAH, RSP, and carbon monoxide. In Figure 2, the results of monitoring inside a veterinarian's office are shown. The major peaks indicate smoking by an office occupant. The fine structure of the decay curve for the cigarette smoke gives a measure of the fine-particle air exchange rate, which we confirmed in other studies. Minor baseline excursions can be related to other activities that occurred in the office, for example, arrival of patients, with accompanying increased outdoor air intrusion and mobile source contributions to the indoor environment.

### **DISCUSSION AND CONCLUSIONS**

Overall, we found the PAH monitor to be a useful instrument, with potential applications in a number of areas. These include: (a) Screening microenvironments for PAH on fine aerosols; (b) Following activities that generate such aerosols; (c) Estimating human exposure to such aerosols; (d) Measuring phase distributions; (e) Following air exchange of fine particles and modeling the air flows; (f) Monitoring for excess PAH aerosols in occupational settings; (g) Monitoring and controlling combustion processes, using the source version of the monitor;<sup>9,16</sup> and (h) Determination of single PAH in emissions with well-characterized profiles, for example, benzo[a]pyrene in environmental tobacco smoke.<sup>9</sup>

Two caveats must be kept in mind in applying this instrument. First, because each individual PAH has a different photoelectric threshold, and because the distribution of total PAH among the various compounds will vary with the source, the monitor is most appropriate as a screening instrument, which produces semi-quantitative results. Despite this caveat, however, the specific responses in a given microenvironment appear to vary precisely with the PAH levels and therefore the monitor is an excellent instrument for following activities. Second, there can be a positive bias from some impurities and non-PAH aerosols, which is highest at high levels of very fine particles. Therefore, to improve the accuracy of the measurements in a given type of microenvironment, the response should be calibrated for the specific source. This can be accomplished by comparisons with integrated sampling. We are examining other means of calibration.

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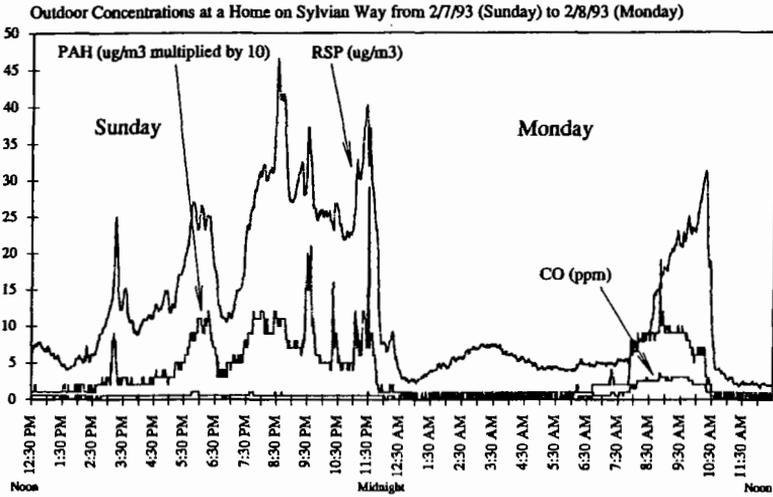


Figure 1. Polycyclic aromatic hydrocarbon (PAH), respirable suspended particles (RSP), and carbon monoxide (CO) concentrations as a function of time in ambient air in a neighborhood in which woodburning fireplaces were in use.

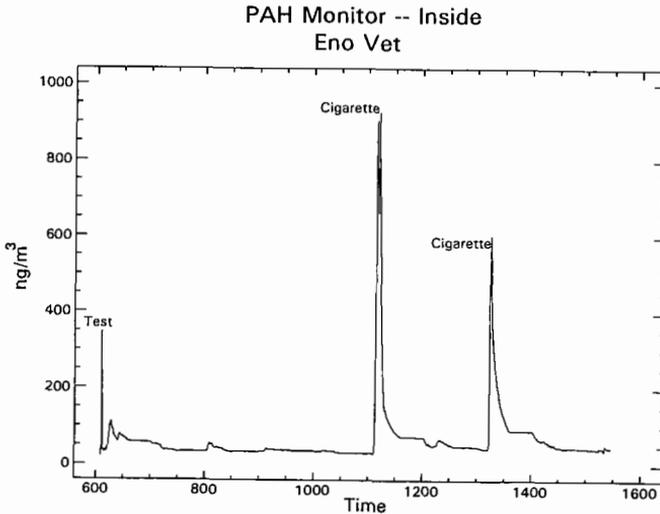


Figure 2. Polycyclic aromatic hydrocarbon (PAH) concentrations as a function of time inside a veterinarian's office in which occupants smoked.

Particle and Gas Transmission Characteristics  
of a VAPS System and Three Different Inlets

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Introduction

Ambient air sampling for the criteria air pollutants is a challenging task. A sampling system capable of collecting both organic and inorganic gases and size-differentiated particles, simultaneously, at remote locations would be a valuable addition to the existing cadre of sampling equipment. An improved sampler referred to as the Versatile Air Pollution Sampler (VAPS) (see Figure 1) was designed for this purpose.

Before the VAPS can be deployed at field sites to do routine ambient air quality monitoring, its physical and chemical performance characteristics need to be confirmed in carefully controlled laboratory studies. A sampling system consisting of one of three different inlets, a VAPS, annular denuders, and filter packs was challenged with solid uranine particles, sulfur dioxide, and nitric acid to determine the system's particle loss characteristics, the 50% aerodynamic particle cut-point ( $d_{50}$ ) of the virtual impactor in the VAPS, the  $d_{50}$  of each inlet, and the gas adsorption characteristics of the entire system. The  $d_{50}$  has been determined for three different inlets: a glass Dichotomous Sampler Type Inlet (DSTI) (see Figure 2), the Slotted Cap Inlet (SCI) (see Figure 3) and a modified version of the University of Minnesota Inlet (UMI) (see Figure 4) sampling in an average wind velocity of 12.3 mph. The  $d_{50}$  of the SCI was also determined while sampling in average wind velocities of 5.3 mph and 9.3 mph. Particle loss in the virtual impactor section of the VAPS was determined through laboratory experiments. Adsorption of  $\text{HNO}_3$ ,  $\text{HNO}_2$ , and  $\text{SO}_2$  by the VAPS, by a PTFE-coated inertial impactor, and by a PTFE-coated metal DSTI was also examined.

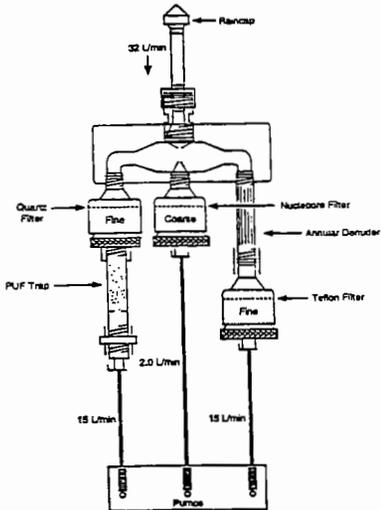


Figure 1 Versatile Air Pollution Sampler (VAPS)

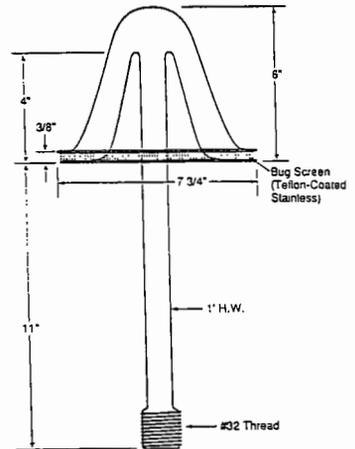


Figure 2 Beckman Dichotomous Sampler Inlet Constructed from Teflon-Coated Glass and Modified for the VAPS (DSTI)



Figure 3 Slotted-Cap Inlet (SCI)

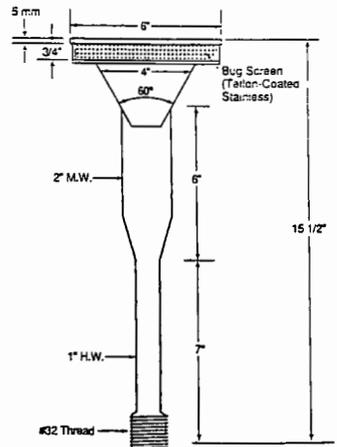


Figure 4 University of Minnesota Inlet Constructed from Teflon-Coated Glass and Modified for VAPS (UMI)

## Experimental Procedures

The particle loss characteristics of the VAPS and the inlets and the  $d_{50}$  of the VAPS virtual impactor and each inlet were determined in a series of controlled laboratory experiments. The VAPS was mounted with each inlet in a specially designed wind tunnel capable of producing equivalent ambient wind speeds between 1.5 and 12.3 mph. For each test, the system was operated at a flow rate of 30 lpm. Monodisperse aerosol particles were generated using a vibrating orifice aerosol generator. The solid uranine particles were continuously injected into the windtunnel upwind of the test section for the duration of each test. Aerodynamic particle diameters used in the study ranged in size from  $3.56 \mu\text{m}$  to  $22 \mu\text{m}$ . The particles and air stream were thoroughly mixed before reaching the test section to insure a uniform particle distribution at the test section. An isokinetic sampling probe was mounted in the test section to measure the particle concentration for each test.

After each test, the inlet section, the VAPS body, and the VAPS top and bottom virtual impactor jets were carefully washed with a known volume of reagent water. The 47-mm filter in the filter pack was completely immersed in a known volume of reagent water. Since the particles used in the study were fluorescent, the solutions were analyzed for total particle mass using a fluorometer. The mass of particles collected in each inlet is reported as a percent of the total particle mass collected by the sampling system. The particle mass lost in the VAPS was calculated as a percent of the total particle mass collected in the VAPS and on the backup filter.

Adsorption of  $\text{HNO}_3$ ,  $\text{SO}_2$ , and  $\text{HNO}_2$  (present in the  $\text{HNO}_3$  solution) by VAPS components and by PTFE-coated DSTI and inertial-impactor inlets was examined by diffusing the gases into purified and filtered room air. The surfaces were then extracted with ion chromatography (IC) eluant and analyzed for nitrite, nitrate, and sulfate by IC. Reagent blanks and system blanks were run and contained negligible amounts of impurities.

For some adsorption tests, the surfaces were lightly coated with Vaseline by immersion in a 10 gm/L suspension of Vaseline in pentane followed by air drying. The effect of scratches in the PTFE coatings was examined by making six deep lengthwise cuts (down to bare metal) with a sharp knife on both the outer and inner surfaces of both the top and bottom jets of a VAPS virtual impactor.

## Discussion of Results

The virtual impactor in the VAPS has a  $d_{50}$  of  $2.40 \mu\text{m}$  aerodynamic particle diameter. Figure 5 shows a plot of the

d50 Determination of Virtual Impactor in VAPS

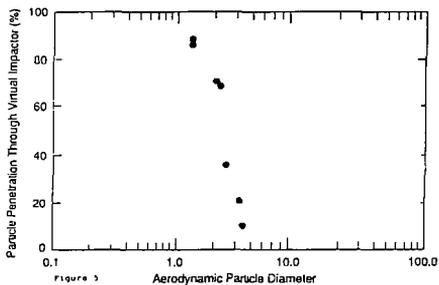


Figure 5

d50 Determination of SCI at Three Wind Speeds

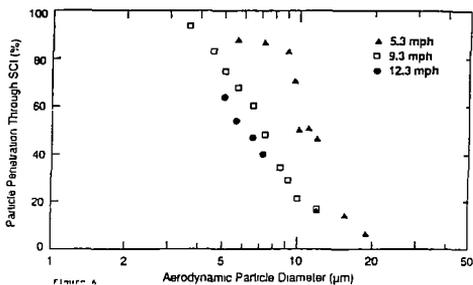


Figure 6

d50 Determination of DSTI Sampling in a 12.3 mph Wind

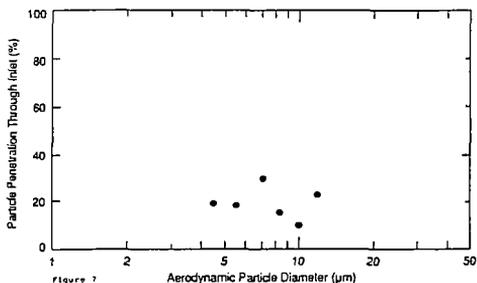


Figure 7

d50 Determination of UMI Sampling in a 12.3 mph Wind

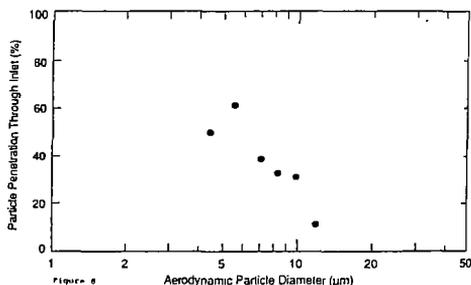


Figure 8

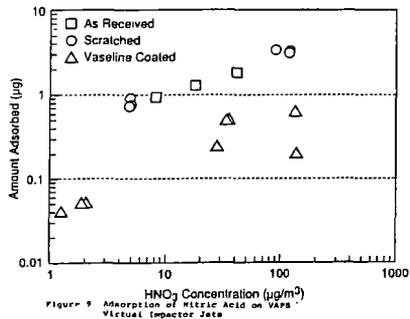


Figure 9 Adsorption of Nitric Acid on VAPS Virtual Impactor Jets

experimental data including all of the particle mass captured in the VAPS, denuders and filter packs. The  $d_{50}$  is sharp and little or no particle loss was found on the virtual impactor jets (see Table 1). Figure 6 shows the  $d_{50}$  experimental results for the SCI sampling in three different wind velocities. At 5.3 mph, the  $d_{50}$  of the SCI is 10.5  $\mu\text{m}$  aerodynamic particle diameter. The cut-point is not sharp (like a jet-type inertial impactor) but it is distinct. At 9.3 mph, the experimental data show that the  $d_{50}$  is 7.0  $\mu\text{m}$  aerodynamic particle diameter, and the cut-point is sharp, much like that of a jet-type inertial impactor. At 12.3 mph, the  $d_{50}$  of the SCI is 6.0  $\mu\text{m}$  aerodynamic particle diameter.

The  $d_{50}$  experimental results for the glass DSTI and the UMI sampling at 12.3 mph are incomplete at this time and should be viewed as preliminary (see Figures 7 and 8). It is evident that the  $d_{50}$  for the glass DSTI will be less than 6.0  $\mu\text{m}$  aerodynamic particle diameter and the  $d_{50}$  of the UMI will be approximately 7.0  $\mu\text{m}$  aerodynamic particle diameter. The true shapes of the performance curves are not discernable from the limited amount of data reported.

**Table 1: Particle Losses in the VAPS Virtual Impactor Section**

Test #	Aerodynamic Particle Diameter ( $\mu\text{m}$ )	Virtual Impactor Section Particle Losses (%)		
		Bottom Jet	Top Jet	Body
20	1.2	0	0	0
18	2.0	0	0	0
15	2.2	0	0	0
17	2.5	1	2	0
22	3.2	5	1	0
16	3.4	0	0	0
19	3.6	2	2	0
12	4.6	0	0	0
14	5.7	0	0	0

The first sets of adsorption tests examined the uptake of  $\text{HNO}_3$  by a VAPS fitted with a PTFE-coated inertial impactor. Significant adsorption (at times exceeding 20% of the  $\text{HNO}_3$  entering the system) occurred and measurable amounts of  $\text{HNO}_3$  were found on all of the system components, including the inlet, the impaction disk (whether oiled or not), the virtual impactor jets, and the main block of the VAPS. Coating of the virtual impactor jets with Vaseline

dramatically reduced uptake of HNO<sub>3</sub>, as did triple-coating them with PTFE (Table 2).

**Table 2: HNO<sub>3</sub> ADSORPTION ON VIRTUAL IMPACTOR JETS**

<u>JETS USED</u>	<u>N</u>	<u>Avg. HNO<sub>3</sub>-N μg/m<sup>3</sup></u>	<u>Percent Adsorbed</u>
"Original Recipe"	7	25.1	2.56 ± 0.96
Triple PTFE Coated	3	45.5	0.18 ± 0.13
Vaseline Coated (Original Jets)	6	31.6	0.06 ± 0.09

In another set of tests, the VAPS was fitted with a PTFE-coated DSTI inlet and exposed to HNO<sub>3</sub>, HNO<sub>2</sub>, and SO<sub>2</sub> simultaneously. Significant losses of HNO<sub>3</sub> and SO<sub>2</sub> occurred, especially at low concentrations (Table 3); but no loss of HNO<sub>2</sub> was observed in these or any other tests. The DSTI was responsible for a majority of the losses.

**Table 3: TRANSMISSION EFFICIENCY AND ADSORPTIVE LOSSES USING THE DSTI INLET WITH THE VAPS SYSTEM**

<u>Expt. No.</u>	<u>HNO<sub>3</sub>-N</u>			<u>SO<sub>2</sub> as Sulfate</u>		
	<u>Conc. μg/m<sup>3</sup></u>	<u>Trans. Eff., %</u>	<u>% Loss on DSTI</u>	<u>Conc. μg/m<sup>3</sup></u>	<u>Trans. Eff., %</u>	<u>% Loss on DSTI</u>
5	5.8	89	62	615	>99	96
6	3.9	90	70	586	>99	81
7	0.3	67	78	5.4	89	96
8	0.3	79	57	4.7	97	88
9	2.3	90	75	1.8	77	96
10	0.3	79	55	1.5	93	75

A recent series of tests examined the uptake of HNO<sub>3</sub> and SO<sub>2</sub> by VAPS virtual impactor cones tested "as received", deeply scratched, and deeply scratched but lightly coated with Vaseline. Adsorption of SO<sub>2</sub> was insignificant in all three sets of tests. The "as received" and deeply scratched jets adsorbed a significant amount of HNO<sub>3</sub>, with the data for both lying on the same adsorption isotherm (Figure 9). Adsorption of HNO<sub>3</sub> increased with increasing concentration, as expected; but the relative losses (expressed as percent loss) were greatest at the lowest concentrations. A light coating of Vaseline on the scratched jets caused a dramatic reduction in HNO<sub>3</sub> adsorption.

## Conclusions

The following conclusions can be drawn from the reported results.

- 1) The  $d_{50}$  of the VAPS virtual impactor is 2.40  $\mu\text{m}$  aerodynamic particle diameter.
- 2) The particle losses in the VAPS are less than 6% and these occur on the virtual impactor jets.
- 3) The  $d_{50}$  of the SCI varies with ambient wind velocity. The largest  $d_{50}$  value is 10.5  $\mu\text{m}$  at an ambient wind velocity of 5.3 mph. At 9.3 mph the  $d_{50}$  drops to 7.0  $\mu\text{m}$  and at 12.3 mph the  $d_{50}$  is 6.0  $\mu\text{m}$ .
- 4) The results reported for the DSTI and the UMI while sampling in a 12.3 mph ambient wind velocity are of a preliminary and incomplete nature. The  $d_{50}$  of the DSTI is less than 6.0  $\mu\text{m}$  and the  $d_{50}$  of the UMI is approximately 7.0  $\mu\text{m}$ .
- 5) Significant adsorption of  $\text{HNO}_3$  by the VAPS and by PTFE-coated DSTI and inertial-impactor inlets was often observed over a broad range of  $\text{HNO}_3$  concentration.
- 6) Virtual impactor jets adsorbed more than 10 times less  $\text{HNO}_3$  when triple-coated with PTFE and more than 30 times less when lightly coated with Vaseline.
- 7) Transmission of  $\text{HNO}_3$  and  $\text{SO}_2$  through the VAPS and a PTFE-coated DSTI ranged from 67 to >99 percent. Values below 90% were associated with low concentration. The DSTI was responsible for the majority of the losses.  $\text{HNO}_2$  was not adsorbed by any of the surfaces studied.
- 8) As the concentration of  $\text{HNO}_3$  decreased, the mass adsorbed on the VAPS virtual impactor jets decreased, but the percentage adsorbed increased. Hence, adsorptive losses are most significant at low concentrations.
- 9) Deeply scratched VAPS virtual impactor jets adsorbed no more  $\text{HNO}_3$  than unscratched jets. Adsorption of  $\text{SO}_2$  was negligible whether or not the jets were scratched.
- 10) A light coating of Vaseline reduced adsorption of  $\text{HNO}_3$  by the VAPS virtual impactor jets by about an order of magnitude.

# Impact of Changes in Sulfate Aerosol Loading on Greenhouse Warming

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## ABSTRACT

When fossil fuel is burned, both CO<sub>2</sub> and SO<sub>2</sub> are injected into the atmosphere. As a result of the Clean Air Act, emissions of SO<sub>2</sub> relative to CO<sub>2</sub> are expected to change. Sulfate aerosols resulting from the gas-to-particle conversion of SO<sub>2</sub> are capable of changing climate by: (1) clear sky radiative effects and (2) modifying the cloud albedo. The latter results from increased cloudiness and larger concentrations but smaller diameter of cloud droplets since sulfate aerosols constitute effective cloud condensation nuclei (CCN). We used diagnostic modeling to simulate the effect of the changes in sulfate aerosol loading on greenhouse warming. Three scenarios, suggested by the Intergovernmental Panel on Climate Change (IPCC), were used. They are: growth of emissions by 2% per year, a reduction by 2% per year, and a "business as usual" scenario of 0% per year. The optical thickness of the cloud was found to be proportional to  $N_c^{1/3}$  where  $N_c$  is the number concentration of cloud droplets. A 2% per year reduction of fossil fuel emissions indicates a 30% reduction in SO<sub>2</sub>-derived cooling in the next 50 years. Two percent growth per year for 50 years will cause a 40% increase in SO<sub>2</sub> derived cooling.

## INTRODUCTION

Emissions of Sulfur Dioxide (SO<sub>2</sub>) from the burning of fossil fuels leads to the presence of sulfate aerosols which influence climate by: (1) clear sky radiative effects and (2) modifying cloud albedo. For clear sky conditions alone, the cooling caused by current emissions rates is estimated<sup>1</sup> to be 1.0 Wm<sup>-2</sup> averaged over the Northern Hemisphere. Observed<sup>2</sup> increases in sulfate derived cloud droplet number concentration indicate a cooling of 2-3 Wm<sup>-2</sup> in eastern North America due to increased reflectivity of clouds. These values are comparable to the estimated<sup>3</sup> 2.5 Wm<sup>-2</sup> heating due to anthropogenic greenhouse gas emissions up to the present. The short residence time of SO<sub>2</sub> and the non-uniform distribution of anthropogenic SO<sub>2</sub> emissions produce regional variation in SO<sub>2</sub>-cooling effects. Future changes in climate forcing due to SO<sub>2</sub> and CO<sub>2</sub> will depend on the variation of emissions of these two gasses relative to one another. Reduction of SO<sub>2</sub> emissions as mandated by the Clean Air Act will cancel cooling due to SO<sub>2</sub>. Because of the short atmospheric lifetime of SO<sub>2</sub>, ambient concentrations will adjust within weeks to changes in emissions. The concentration of CO<sub>2</sub>, however, will continue to rise for more than a century even if emissions are kept constant at present levels. It is for this reason the question has been asked, "Will reducing the emissions of fossil fuels cause global warming?"

Wigley<sup>4</sup> has attempted to determine the sensitivity of the climate system to changes in the emission of both carbon dioxide and sulfur dioxide. The Intergovernmental Panel on Climate Change (IPCC), in their assessment of global climate change, have recognized the importance of carbon dioxide from fossil fuel emissions in climate change. They have proposed three scenarios of change in concentration of atmospheric carbon dioxide. These scenarios are growth of emissions by 2 percent per year, a reduction of two percent per year, and a "business as usual" scenario of zero growth per year. Wigley<sup>4</sup> uses the carbon dioxide concentration scenarios of the IPCC and the forcing-concentration relationship of the IPCC<sup>5</sup> Working Group 1 to determine climate sensitivity to simultaneous changes in CO<sub>2</sub> and SO<sub>2</sub>. In his analysis, a diagnostic model of global climate change based on direct radiative effects of SO<sub>2</sub> in the clear atmosphere and indirect effects of SO<sub>2</sub> in the atmosphere as a modifier of cloud albedo was developed. The role of SO<sub>2</sub> in the formation of hygroscopic sulfate aerosol is well known as is their capability of increasing the reflectivity of low level clouds<sup>6,7,8</sup>. This increase in reflectivity in turn produces a cooling effect on the earth-troposphere system. It is suggested that regionally SO<sub>2</sub> derived cooling is currently counteracting the warming produced by carbon dioxide. The greenhouse warming of the earth-troposphere system caused by doubling of CO<sub>2</sub> could be counteracted by a meager 2% increase in the shortwave albedo of the low level cloud cover around the globe. Such a change could be initiated<sup>9</sup> by a four fold increase in CCN concentration.

## CLIMATE MODEL

Wigley<sup>4</sup> has developed a simple diagnostic model to determine the sensitivity of the climate system to changes in the emission of SO<sub>2</sub>. If dE represents the change in SO<sub>2</sub> emissions, the clear-sky direct radiative forcing dQ<sub>d</sub> may be considered as linearly related to dE:

$$dQ_d = adE. \quad (1)$$

For the indirect SO<sub>2</sub> effect through cloud mediated albedo changes, dQ<sub>i</sub> ∝ dC/C, where C represents CCN number concentration. Assuming that changes in C are linearly related to changes in SO<sub>2</sub>-related aerosol concentration, we may write

$$dQ_i \propto dE/E = b dE/E. \quad (2)$$

Here a and b are constants of proportionality whose magnitude should be determined through experiments. However, uncertainties in a and b are avoided by Wigley<sup>4</sup> by expressing future radiative forcing changes in terms of present manmade SO<sub>2</sub>-related forcing(δQ<sub>0</sub>):

$$\delta Q_i = \delta Q_0 \frac{\ln[E_0/E_1 + (1 - E_0/E_1)\exp(\alpha t)]}{\ln[E_1/E_0]} \quad (3)$$

where E<sub>0</sub> is the natural background emission rate, E<sub>1</sub> is the current total emission rate (at time t = 0) and α is the growth rate of emissions. The growth rate α is taken from the three previously mentioned scenarios of the IPCC.

The result of Wigley's model (Fig. 1) shows that a reduction in the emission of fossil fuel will cause a positive SO<sub>2</sub>-related radiative forcing change. This will lead to global warming by CO<sub>2</sub>. There will no longer be a SO<sub>2</sub>-derived cooling to counteract greenhouse warming by CO<sub>2</sub>.

In the development of his model, Wigley<sup>4</sup> assumes a linear relationship between SO<sub>2</sub> emissions, CCN concentrations, and cloud droplet concentrations. Another relationship that was assumed linear by Wigley<sup>4</sup>, the relationship between cloud reflectivity and cloud droplet concentration, is non-linear. We have developed a new model utilizing Wigley's modeling technique that includes the non-linear relationship between cloud reflectivity and cloud droplet concentration to determine the change in cloud radiative forcing due to changes in SO<sub>2</sub> emissions.

If, like Wigley, we assume that there is a linear relationship between SO<sub>2</sub> emissions, CCN concentrations, and cloud droplet concentrations, then the size of cloud droplets will become smaller with increased SO<sub>2</sub> emissions. The reasoning for smaller cloud droplets is that compared to clouds formed under similar conditions, those clouds formed with air masses of increased CCN content have smaller cloud droplets because the available water vapor will be shared by more cloud condensation nuclei that are activated in a cloud. Reduced cloud droplet size in clouds formed with invariant liquid water content implies increased cloud droplet concentration. Cloud droplet size influences cloud albedo. A large change in cloud albedo with a small change in cloud droplet radius is due to a non-linear relationship between cloud droplet concentration and cloud albedo. The albedo of the cloud, A<sub>c</sub>, can be evaluated in terms of the optical depth<sup>10</sup> as

$$A_c = \tau / (7.7 + \tau). \quad (4)$$

Optical depth, τ, is related to the number of cloud droplets, N<sub>c</sub>, the cloud liquid water content, q<sub>c</sub>, the cloud thickness, H, and the density of liquid water ρ<sub>w</sub> by the relationship<sup>7</sup>

$$\tau = H[9\pi(q_c)^2 N_c / (2\rho_w^2)]^{1/3} \quad (5)$$

As cloud droplet size is reduced (Fig 2), with invariant cloud liquid water, the albedo of the cloud increases. In Fig. 3 cloud albedo is shown as a function of cloud droplet concentration. Using the non-linear relationship would alter Wigley's estimation of the future indirect effect of SO<sub>2</sub> on global climate.

The number concentration of cloud droplets, N<sub>c</sub> is linearly related to the of CCN concentration in an air mass but the relationship is not a simple one<sup>11</sup>. For our model let us suggest the relationship

$$N_c = a N_{CCN} \quad (6)$$

where  $a$  is a percent of CCN activated as cloud droplets and is a function of the characteristics of the air mass that formed the cloud.

In the case of conversion of  $\text{SO}_2$  into sulfate aerosol, Wigley assumes that  $\text{SO}_2$  will be converted directly into CCN and ignores the physics of the mechanisms by which this conversion takes place in the atmosphere. In the aqueous production of sulfate from  $\text{SO}_2$ , there exists a limiting factor, namely, the pH of the cloud water. If the cloud water pH is less than four the conversion<sup>12</sup> of  $\text{SO}_2$  into sulfate will be negligible, regardless the concentration of  $\text{SO}_2$ . It is with this limitation that we will relate the number of CCN to the emissions of  $\text{SO}_2$  by

$$N_{\text{CCN}} = bE_{\text{SO}_2} \quad (7)$$

where  $b$  is the percent of  $E_{\text{SO}_2}$  that will be converted into sulfate CCN through cloud processes.

With these new considerations we can use Wigley's modeling approach to determine future indirect  $\text{SO}_2$ -related climate forcing. Let us consider future  $\text{SO}_2$  emissions as determined by an equation of the form

$$dE_{\text{SO}_2} = E_0 e^{\alpha t} \quad (8)$$

where  $dE_{\text{SO}_2}$  is future emissions,  $E_0$  is the current rate of emissions and  $\alpha$  is the growth rate.

For the indirect  $\text{SO}_2$  effect through cloud albedo, utilizing equation 5 we can write

$$dQ = (dN_c)^{1/3} \quad (9)$$

Equations (6) and (7) imply that the droplet concentration can be rewritten in the indirect equation as

$$dQ = (a b dE_{\text{SO}_2})^{1/3} \quad (10)$$

and by applying the emissions growth equation (8) we find that

$$dQ = (a b E_0 e^{\alpha t})^{1/3} \quad (11)$$

We can rid ourselves of the uncertainties in the values of  $a$  and  $b$  by expressing the future forcing changes in terms of the present day  $\text{SO}_2$  forcing  $Q_0$

$$dQ = Q_0 e^{\alpha t/3} \quad (12)$$

If we manipulate the equation to

$$\frac{dQ}{Q_0} = e^{\alpha t/3} \quad (13)$$

then climate change in the form of cloud climate radiative forcing can be expressed as a percent change from the present without the need to calculate any current cloud radiative forcing values.

If we apply equation (13), the ratio of the values of future cloud climate radiative forcing to present day cloud climate radiative forcing can be found for 50 years from the present. Selecting  $\alpha$  equal to +2 percent per year and -2 percent per year to represent an  $\text{SO}_2$  growth scenario and a  $\text{SO}_2$  reduction scenario respectively we can examine the sensitivity of the climate system to changes in the emissions of fossil fuel derived  $\text{SO}_2$ .

## CONCLUSIONS

Figure 1. shows the result of the new model with those of Wigley. A two percent per year reduction in the emissions of  $\text{SO}_2$  would reduce the  $\text{SO}_2$ -related radiative forcing by clouds resulting in warming. A two percent per year growth of emissions would produce a much larger growth in radiative forcing by clouds, resulting in cooling. The results of the new model differ from the results of Wigley (1991) due to the application of the non-linear relationship between cloud reflectivity and cloud droplet concentration. The application of the non-linear relationship decreases the magnitude of the aerosol contribution to climate forcing. Table 1 shows the combined  $\text{CO}_2$  and  $\text{SO}_2$  forcing changes for the Northern Hemisphere as calculated by Wigley. Table 2 shows the combined  $\text{CO}_2$  and  $\text{SO}_2$  forcing changes calculated by the new model. Wigley estimated, over the next 10-30 years, that it is the aerosol

effect that will influence changes in total forcing, to the extent that reduced emissions produce a larger forcing increase, thus a larger global warming than increased emissions. The new model verifies these conclusions. It is several decades before any noticeable radiative forcing response to any emission policy occurs, due to the large response time of the carbon cycle. The aerosol effect delays this response. The emission control scenarios show increases in forcing changes (warming) depending on the strength of the aerosol effect,  $\Delta Q_0$ . This tendency would be exacerbated by any  $\text{SO}_2$ -specific emissions controls as those mandated by the Clean Air Act. Even a small aerosol effect would delay the response of the climate system to attempts to control or limit the greenhouse problem. Given the regional nature of  $\text{SO}_2$  cooling, regional climate is more susceptible to forcing changes than the global climate.

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Table 1. Combined CO<sub>2</sub> and aerosol forcing changes in the Northern Hemisphere for different emissions growth rates and different strengths of the aerosol effect ( $\Delta Q_0$ ).

Emissions growth rate ( $\alpha$ )	$\Delta Q_0$ ( $W\ m^{-2}$ )	Year										
		2000	2010	2020	2030	2040	2050	2060	2070	2080	2090	2100
+2% yr <sup>-1</sup>	0.0	0.36	0.77	1.25	1.80	2.43	3.14	3.94	4.84	5.74	6.69	7.64
	-0.5	0.27	0.59	0.95	1.37	1.84	2.36	2.95	3.59	4.22	4.75	5.26
	-1.0	0.19	0.41	0.66	0.94	1.25	1.59	1.96	2.34	2.66	2.82	2.88
	-1.5	0.10	0.22	0.36	0.51	0.66	0.82	0.97	1.09	1.10	0.89	0.50
0% yr <sup>-1</sup>	all	0.30	0.58	0.83	1.06	1.27	1.47	1.67	1.85	2.03	2.20	2.37
-2% yr <sup>-1</sup>	0.0	0.26	0.43	0.53	0.59	0.63	0.64	0.63	0.61	0.58	0.55	0.51
	-0.5	0.33	0.56	0.72	0.83	0.90	0.95	0.97	0.98	0.97	0.96	0.94
	-1.0	0.40	0.70	0.91	1.07	1.18	1.26	1.31	1.35	1.36	1.37	1.36
	-1.5	0.48	0.83	1.10	1.30	1.46	1.57	1.65	1.71	1.75	1.77	1.78

For  $\alpha = 0\% \text{ yr}^{-1}$  (middle panel) the aerosol effect is zero and the values shown are therefore those for CO<sub>2</sub> alone. Similarly, for any a value, the aerosol effect is zero for  $\Delta Q_0 = 0 \text{ Wm}^{-2}$ . These rows therefore give the effect of CO<sub>2</sub> alone for  $\alpha \neq 0\% \text{ yr}^{-1}$ . They also give the changes assumed for the Southern Hemisphere.

Table 2. Combined CO<sub>2</sub> and aerosol forcing changes in the Northern Hemisphere for different emissions growth rates and different strengths of the aerosol effect ( $\Delta Q_0$ ).

Emissions growth rate ( $\alpha$ )	$\Delta Q_0$ ( $W\ m^{-2}$ )	Year										
		2000	2010	2020	2030	2040	2050	2060	2070	2080	2090	2100
+2% yr <sup>-1</sup>	0.0	0.36	0.77	1.25	1.80	2.43	3.14	3.94	4.84	5.74	6.69	7.64
	-0.5	0.32	0.7	1.14	1.65	2.23	2.89	3.15	3.42	4.14	4.93	5.75
	-1.0	0.29	0.63	1.03	1.5	2.04	2.65	3.05	3.35	3.57	3.75	3.82
	-1.5	0.25	0.56	0.92	1.35	1.84	2.4	1.76	1.52	1.38	1.10	0.89
0% yr <sup>-1</sup>	all	0.30	0.58	0.83	1.06	1.27	1.47	1.67	1.85	2.03	2.20	2.37
-2% yr <sup>-1</sup>	0.0	0.26	0.43	0.53	0.59	0.63	0.64	0.63	0.61	0.58	0.55	0.51
	-0.5	0.29	0.49	0.62	0.71	0.78	0.73	0.82	0.82	0.81	0.79	0.77
	-1.0	0.33	0.55	0.71	0.83	0.91	0.97	1.00	1.02	1.03	1.04	1.03
	-1.5	0.37	0.61	0.8	0.95	1.07	1.14	1.19	1.23	1.26	1.27	1.29

For  $\alpha = 0\% \text{ yr}^{-1}$  (middle panel) the aerosol effect is zero and the values shown are therefore those for CO<sub>2</sub> alone. Similarly, for any a value, the aerosol effect is zero for  $\Delta Q_0 = 0 \text{ Wm}^{-2}$ . These rows therefore give the effect of CO<sub>2</sub> alone for  $\alpha \neq 0\% \text{ yr}^{-1}$ . They also give the changes assumed for the Southern Hemisphere.

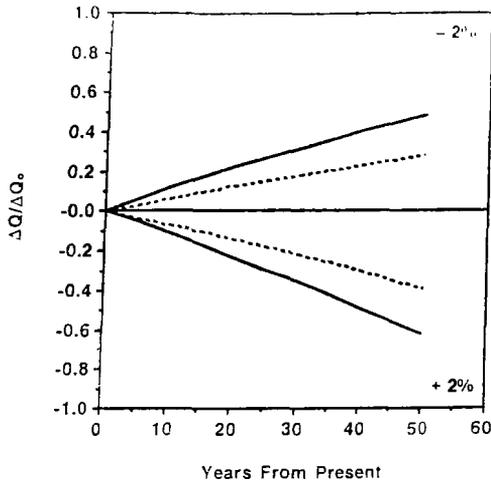


Figure 1. Northern Hemisphere  $\text{SO}_2$ -related forcing changes for emissions growth rates of  $+2\% \text{ yr}^{-1}$  (lower curves) and  $-2\% \text{ yr}^{-1}$  (upper curves) as calculated by Wigley<sup>3</sup>. The full lines represent the indirect (CCN) effect for a present to pre-industrial  $\text{SO}_2$  emissions ratio<sup>1</sup> ( $E_1/E_0$ ) of 3.6. The dashed lines represent the indirect (CCN) effect incorporating the non-linear nature of the relationship between cloud droplet concentration and cloud reflectivity.

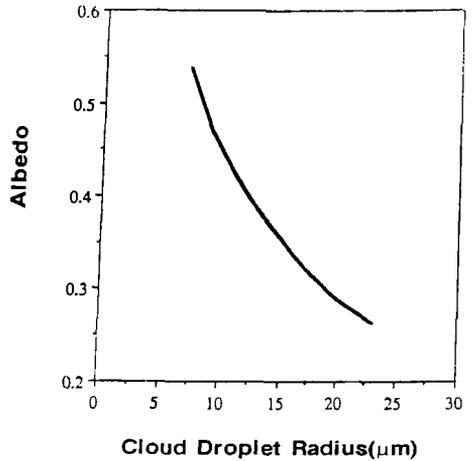


Figure 2. Cloud Albedo vs. Cloud Droplet Radius in micrometers for a cloud of liquid water content of  $0.3 \text{ gm}^{-3}$  and 200m thickness.

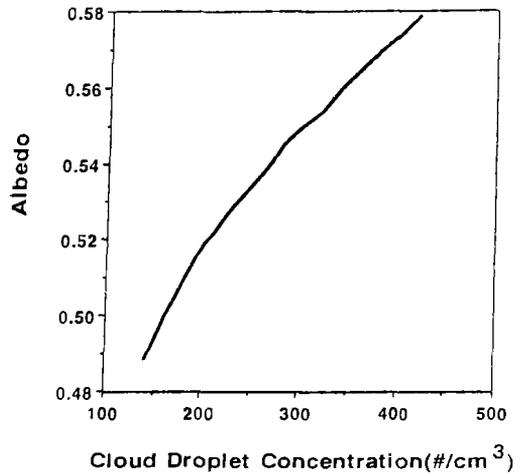


Figure 3. Cloud Albedo vs. Cloud Droplet Number Concentration in  $\text{cm}^{-3}$  for a cloud of liquid water content of  $0.3 \text{ gm}^{-3}$  and 200m thickness.

## Testing Of A Triple-Path Denuder Designed For Quantitative Sulfate And Nitrate Measurements

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### ABSTRACT

A triple-path denuder (TPD) assembly has been tested at the Research Triangle Institute and at the South Dakota School of Mines and Technology. Denuder coatings included oxalic acid for removal of ammonia, and NaCl for capture of nitric acid; a third path was left uncoated. Denuder cassettes contained teflon or acid-washed "quartz" filters, and contained either a blank filter, or were loaded with solid reacting materials such as oxalic acid, NaCl, or MgO (at SDSM&T only). Primary aerosol concentrations of  $(\text{NH}_4)_2\text{SO}_4$  (17 and 79  $\mu\text{g m}^{-3}$ ),  $\text{NH}_4\text{NO}_3$  (10  $\mu\text{g m}^{-3}$ ), and  $\text{H}_2\text{SO}_4$  (10-20  $\mu\text{g m}^{-3}$ ) and of gaseous  $\text{NH}_3$  (12-26  $\mu\text{g m}^{-3}$ ) and  $\text{HNO}_3$  (7-131  $\mu\text{g m}^{-3}$ ) were introduced into the system. Monitoring of generated species was conducted using ion chromatography, and analysis of reactions on denuder coatings and filter loads was completed by x-ray diffraction. Results indicate that losses of  $\text{HNO}_3$  were too large to permit using the TPD for ambient nitric acid reaction product measurements. However, primary sulfate and possibly nitrate aerosol measurements may be completed with this system. Lower limits of detection (LLD) for products in the filter loads for this system vary from less than 0.1% by weight, to as high as 24% for extremely light filter loadings.

## 1. INTRODUCTION

A denuder instrument for stripping of unwanted gaseous species and for protection of collected particulate from artifact formation was designed and given preliminary testing at the South Dakota School of Mines and Technology (Davis *et al.*<sup>1</sup>). Additional testing at the Research Triangle Institute (RTI) was completed in the summer of 1991 (Hodson, *et al.*<sup>2</sup>) for the purpose of introducing controlled atmospheres containing particulate ammonium sulfate (Mascagnite -  $(\text{NH}_4)_2\text{SO}_4$  - "MS"), ammonium nitrate ( $\text{NH}_4\text{NO}_3$  - "AN"), particulate  $\text{H}_2\text{SO}_4$ , and gaseous  $\text{HNO}_3$ , into the denuder system. The purpose of the RTI test was to generate limits of detection data and observe artifact reactions for collected species frequently observed in heavily polluted urban atmospheres sampled at near-ambient concentration levels. The present paper describes a portion of these tests; those for which ammonium sulfate and ammonium nitrate were generated for direct collection on teflon membrane filters.

## 2. DENUER DESCRIPTION AND EXPERIMENTAL DESIGN

The details of the triple-path denuder (TPD) construction have been presented by Davis *et al.*<sup>1</sup>. The instrument was modified by outfitting both paths A and C with Possanzini concentric tube denuders (Possanzini, *et al.*<sup>3</sup>); path B consisted of two concentric tubes of equivalent size, but untreated. The exterior surface of the interior tube and interior surface of the outer tube of the Path A denuder were coated with oxalic acid for the tests described here. Path C was not used for the sulfate and nitrate particulate tests.

Teflon filters (PTFE, 37-mm diam., 2- $\mu\text{m}$  pore) were used exclusively for collections of the nitrate and sulfate aerosols. The loads were concentrated by means of a machined teflon reducer into a 2.5-cm diameter central area of each filter. Blank and loaded filters were weighed at RTI (MS set) and at both SDSM&T and RTI (AN set). For XRD analysis each filter was cemented onto the 2.5-cm diameter spinning pedestal of the x-ray diffractometer. The diffractometer used was a Philips unit with vertical goniometer, graphite monochromator, and automatic divergence slits. Scans were made with a  $\text{CuK}\alpha$  target operated at 40 kV and 20 mA; scan parameters were 0.02-degree step and 4.12-second dwell.

Figure 1 illustrates the configuration of the aerosol generation "tent" and TPD inlet. The tent was constructed of Tedlar, and was supported on a teflon tubing frame. It contained a mixing chamber to combine gaseous and aerosol samples prior to entry into the  $\text{PM}_{10}$  TPD sampling head. For quality assurance (QA) purposes RTI located filter pack cassettes on two sides of the tent; the SDSM&T QA filter pack cassette (CC) was located just above RTI filter cassette B. The aerosols of MS and AN were generated with a TSI Model 3076 atomizer. Aerosol particles were passed through a Kr 85 particle charge neutralizer prior to entrance into the dilution manifold (not shown in Fig. 1).

## 3. QUALITY ASSURANCE

QA measures were taken at all stages of the testing. The general features consisted of:

1. Preliminary XRD scans of blank filters and loaded filters (at simulated ambient concentrations) prior to RTI testing.
2. Novaculite standard QA scans to verify instrument performance during the XRD data analysis stage of the project.

3. Filter weight checks at both the SDSM&T laboratories and at RTI during TPD testing

4. Ion chromatographic (IC) analysis of sampled  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  aerosols, of filter blanks, and of collections at cassette points A and B; and IC solution checks needed for determination of RTI laboratory precision.

A study of the repeatability of the electronic balances used demonstrate that the precision for a given reading may not be better than about 50 micrograms ( $10 \mu\text{g cm}^{-2}$  for the load coverage here), although the balance scales were readable to  $10 \mu\text{g}$  at SDSM&T and  $1 \mu\text{g}$  at RTI.

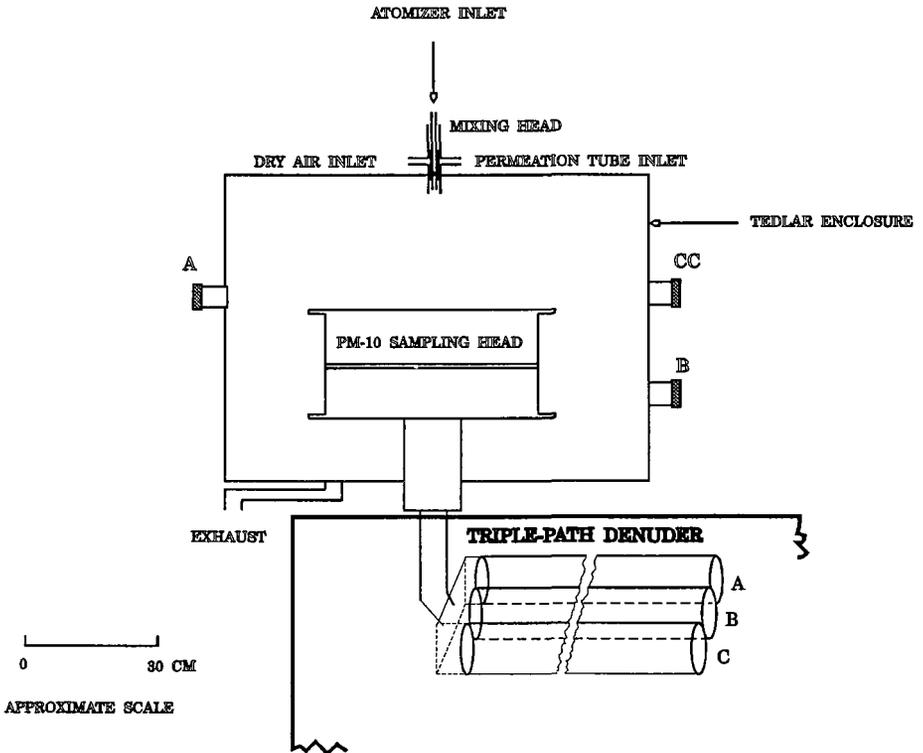


Fig. 1. Physical Arrangement of Triple-Path Denuder Testing

#### 4. RESULTS

##### 4.1 Mascagnite $(\text{NH}_4)_2\text{SO}_4$

Table 1 presents the concentration and flow data for the MS and AN aerosols provided to the TPD according to RTI specifications. The initial MS series target concentration of  $27 \mu\text{g m}^{-3}$  was not achieved, apparently because of excessive losses through the nebulizer system; therefore this target value was increased to the  $80 \mu\text{g m}^{-3}$  given in Table 1. The flow rate at the control cassette ranged from  $0.2 - 0.25 \text{ m}^3 \text{ hr}^{-1}$  whereas the flow rate for the denuder paths A and B ranged from  $1.6$  to  $1.8 \text{ m}^3 \text{ hr}^{-1}$ .

TABLE 1. Delivery and LLD Parameters for Control (CC) and Denuder Samples

PARAMETER	AMMONIUM SULFATE (MS)			AMMONIUM NITRATE (AN)		
Source Concentration	0.02M $(\text{NH}_4)_2\text{SO}_4$			0.015M $\text{NH}_4\text{NO}_3$ + 3000 $\text{ng min}^{-1} \text{NH}_3$		
Target Concentration	$80 \mu\text{g m}^{-3}$			$27 \mu\text{g m}^{-3}$		
Actual Concentration	$79.2 \mu\text{g m}^{-3}$			$10.3 \mu\text{g m}^{-3}$		
Control/Path Data	Time	Mass $\mu\text{g cm}^{-2}$	LLD Percent	Time	Mass $\mu\text{g cm}^{-2}$	LLD Percent
Control (CC)	1 Hr	7.94	----	1 Hr	BBS <sup>1</sup>	----
Path A	1 Hr	30.4	22.3	1 Hr	BBS	5.6
Path B	1 Hr	17.7	3.1	1 Hr	BBS	----
Control (CC)	2 Hr	7.33	----	3 Hr	7.74	----
Path A	2 Hr	96.8	18.5	3 Hr	18.9	5.5
Path B	2 Hr	30.1	1.5	3 Hr	BBS	----
Control (CC)	4 Hr	17.1	---	6 Hr	0.2	----
Path A	4 Hr	184.2	5.4	6 Hr	56.8	2.2
Path B	4 Hr	50.1	0.9	6 Hr	22.6	----

<sup>1</sup> Below Balance Sensitivity (Mass)

Collection was made for 1-, 2-, and 4-hour periods through paths A and B. The ratio of volumes sampled at the path A and B cassettes to that of the control cassette (CC) is generally between 6.5 and 9; When this ratio is taken into account the control cassette mass collected *equivalent* to the path A and B collection under identical flow rates was usually significantly greater for the path B cassette, but often *less* than that for the path A cassette. For example, for the MS 2-hour test the equivalent CC mass was  $60.1$  and  $64.1 \mu\text{g cm}^{-2}$ , respectively, for paths A and B, compared to the actual measured  $96.8$  and  $30.1 \mu\text{g cm}^{-2}$  for paths A and B cassettes. This suggests either

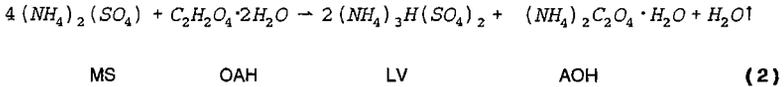
excessively large losses of aerosol along the route to the path B filter or an additional source of mass arriving at the path A filter. Evidence from the type of compounds observed suggests that particles from the path A denuder coating were dislodged and collected on the path A cassette substrate. This point will be discussed further below.

In most cases sufficient collection of MS aerosol at the path A and B cassettes was obtained to determine the limits of detection for the XRD scanning conditions attempted. The lower limits of detection (LLD) for a component can be determined by several methods (Davis<sup>4</sup>). For a single component, such as required in these analyses, the LLD is given by the simple 3- $\sigma$  criterion

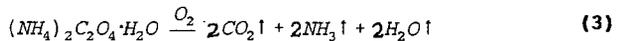
$$LLD = 300 W_j \frac{\sqrt{I_{bg}^\alpha}}{I_j^\alpha} \quad (1)$$

where  $I_{bg}^\alpha$  is the *integrated* background intensity measured beneath the component *integrated* peak intensity  $I_j^\alpha$ , and for these samples,  $W_j = 1$ . The LLD here is given as weight percent of the specific mass (*Mass* of Table 1) for each filter collection. Figure 2 presents the LLD values and intensity variations of the sum of the 102,111 and 103 peaks versus atmosphere sampled and specific mass for the three test periods.

The initial XRD scans of these collections were made on 9 Sept. 1991, shortly after completion of the RTI field testing in mid-August. The sample collected for the 4-hour path A run was scanned again on 17 April, 1992 and finally again on 22 Feb. 1993. This final "aged" sample contained 44.7% mascagnite and 55.3% letovicite as determined from the XRD analysis, using reference intensity methods of Davis *et al.*<sup>4</sup>. The first scan demonstrated poorly crystalline MS along with unidentified peaks which were first thought to be an oxalate or oxalate hydrate, possibly ammoniated, that resulted from spalling from the oxalic acid hydrate coatings of the path A denuder. Subsequent scans revealed an increase of the MS 102 peak from 5 to 50 to 80 cps along with sharpening up of all peaks sufficiently to recognize the formation of letovicite,  $(NH_4)_3H(SO_4)_2$ , an acid species of ammonium sulfate. The presence of oxalates have never been confirmed on any of these patterns; The presence of letovicite, however, strongly implies contamination of the path A mascagnite collection and reaction according to

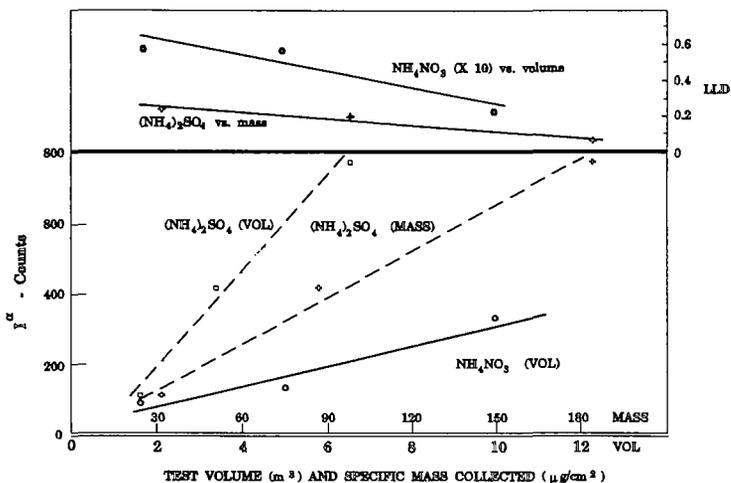


and where the ammonium oxalate, a transient phase, is presumed to further dissociate to gaseous components:



We have also discovered that grinding a mixture of mascagnite and oxalic acid hydrate quickly converts the mascagnite to letovicite. Such a conclusion might even suggest that oxalic acid hydrate is not an appropriate choice for denuder coatings in contact with freshly generated ammonium-bearing test aerosols because of possibility of removal of stabilizing ammonia from the sampled atmosphere.

**AMMONIUM SULFATE AND AMMONIUM NITRATE ON TEFLON (PTFE)  
PATH A SERIES**



**Figure 2. Diffraction Intensity for Selected Peaks vs. Mass and Volume and LLD values for Ammonium Sulfate and Nitrate Aerosols.**

**4.2 Ammonium Nitrate NH<sub>4</sub>NO<sub>3</sub>**

Table 1 and Figure 2 present the comparable data from these tests for ammonium nitrate (AN). An attempt was made to maintain AN aerosol stability with an excess of NH<sub>3</sub> gas during loading, even though most of the excess would be lost to the oxalic acid denuder coating for path A collections. The QA checks of these runs showed a high relative standard deviation for the AN atmosphere concentration of 34.3%. The final filter weighings showed little or no mass accumulation above the sensitivity of the balance. However, weak but distinct peaks for the strongest diffraction spacing of AN were recognizable on most of the filters. LLD values were thus obtained for the A-path collections. In contrast to the MS series of tests, both ammonium hydrogen oxalate hydrate (AHOH), NH<sub>4</sub>HC<sub>2</sub>O<sub>4</sub>•H<sub>2</sub>O, and ammonium oxalate hydrate (AOH), (NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub>•H<sub>2</sub>O, were found to exist with the expected NH<sub>4</sub>NO<sub>3</sub>. Analysis of the path A filters for these three components is presented in Table 2. For purposes of correction of intensities for transparency and matrix effects for the 1-hour collection, a specific mass level of 200 μg cm<sup>-2</sup> was assumed since no weight could be detected from the balance measurements (BBS, Table 1).

**TABLE 2 XRD PHASE ANALYSIS OF NH<sub>4</sub>NO<sub>3</sub> SERIES COLLECTIONS**

FILTER COLLECTION PERIOD	COMPONENT WEIGHT PERCENT AND VARIANCE ERRORS		
	AN	AHOH	AOH
1-HOUR	19.9 ± 2.5	48.6 ± 4.7	31.5 ± 4.4
3-HOUR	26.4 ± 3.1	55.2 ± 4.4	18.4 ± 3.6
6-HOUR	12.7 ± 1.6	78.7 ± 2.6	8.6 ± 2.0

These analyses demonstrate conclusively that contamination from the denuder coatings exists on the teflon filter collections. The one B-path collection showing sufficient mass for XRD analysis revealed only the AN phase peak present, as expected.

## 5. DISCUSSION AND CONCLUSIONS

The tests of the triple-path denuder described here have great value in providing direction for future work with this type of system. First, comparison of control and sample cassette loads strongly suggests losses of particulate that may result both from surface scavaging through the system conduit parts and control losses from incomplete gas-to-particle conversion. Loads obtained at near-ambient concentrations proved marginal for XRD analysis; masses collected on many of the filters were below the measurement range of the electronic balances used. However, XRD patterns, obtained under slow scanning conditions, can still be obtained so that LLD values could be calculated. Considering the 10-80  $\mu\text{g m}^{-3}$  concentrations used here it is apparent that good XRD patterns can be achieved in an ambient sampling environment only after several hours continuous operation of the system. Use of oxalic acid as a denuder coating for  $\text{NH}_3$  removal is not recommended because of the likely losses from denuder walls to collection cassette.

## 6. ACKNOWLEDGEMENTS

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***Session 12***

***Risk Assessment***

**Assessment of Ambient-Air Quality at Landfills 8 and 10 of**

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**ABSTRACT**

Five rounds of ambient-air sampling were conducted between July and October 1991 at Landfills 8 and 10 of Wright-Patterson Air Force Base (WPAFB), Ohio. The primary air monitoring objectives were to determine whether the landfills are emitting contaminants into ambient air and to assess the environmental impact based on the existing National Ambient Air Quality Standards (NAAQSs) and the State of Ohio guidelines. WPAFB is located in southwestern Ohio, east of Dayton (Figure 1). Nine sampling sites, including an upwind and a collocated sampling site, were used during each round of sampling (Figure 2). Particulate matter below 10 microns (PM-10) and selected metals, volatile organic compounds (VOCs), and semi-volatile organic compounds (SVOCs) were measured at each sampling site. All the sampling equipment has been designated as the reference method or equivalent by the U.S. Environmental Protection Agency (USEPA).

Seventeen VOCs, 10 SVOCs, and 10 metals were detected in five rounds of sampling. Of 17 VOCs, methane was detected at all sampling sites in each round; the highest concentration of methane was detected at Landfill 10. Relatively high concentrations of acetone and benzene were measured at several sampling sites. Among 10 SVOCs, fluoranthene, naphthalene, and phenanthrene were detected at almost all sampling sites in all sampling rounds. The concentrations of SVOCs detected at upwind and downwind sites were of the same order of magnitude. Among the 10 metals, copper was detected at virtually all sampling sites.

In spite of wide variation in the particulate concentrations from round to round, the PM-10 concentration never exceeded the NAAQS of 50 micrograms per cubic meter ( $\mu\text{g}/\text{m}^3$ ) of air.

Based on the results of five rounds of air sampling, no deterioration of ambient-air quality due to emission of landfill gases was observed.

## INTRODUCTION

Landfills 8 and 10 are among the several sites targeted for remediation at WPAFB. Both landfills are located in the southern portion of WPAFB (Figure 1). Landfill 8 was operated from 1947 until the early 1970s, whereas Landfill 10 was operated from 1965 to early 1970s. Both landfills were reportedly used for the disposal of general refuse consisting of oily wastes, organic and inorganic wastes, hospital waste, toxic and hazardous waste, and acid neutralization. Little is known about the waste quantities and disposal dates. At both landfills, waste was disposed of in a trench-and-cover operation. Both landfills were reportedly covered with clay or soil caps of varying thickness. The cap over Landfill 8 is moderately vegetated with grasses and varies in thickness from 3 to 12 feet, averaging typically 8 to 10 feet over the majority of the landfill. The cap over Landfill 10 is sparsely vegetated with grasses and varies in thickness from 1 to 8 feet, with a typical average of 2 feet over most of the landfill. The respective elevations of Landfill 8, Landfill 10, and the valley between the landfills are 945, 910, and 860 feet above the National Geodetic Vertical Datum (NGVD) of 1929.

The natural topography of the area has been extensively modified through waste disposal at both landfills, by the construction of personnel housing in the area, and the construction of bunkers for ordnance storage at numerous locations in the valley between the landfills. The bunkers have since been removed. When residential housing was being built around the landfills from 1971 to 1973, the surface of Landfill 8 was developed into a recreational area. The valley between the landfills was closed to vehicular traffic and was developed into a wooded park with footpath access to both landfills.

Parts of both landfill areas were used for recreational purposes from the mid-1970s to early 1985 when parts of those landfill areas were fenced and posted off-limits. All of the landfill areas and the intervening valley were fenced in 1986 and warning signs were placed.

Since WPAFB was included on the National Priorities List (NPL), Remedial Investigations (RIs) and Feasibility Studies (FSs) are being conducted under the guidance of U.S. Environmental Protection Agency (USEPA) Region V and the Ohio Environmental Protection Agency (OEPA).

Several investigative studies have been performed since 1982 at both landfill sites. Engineering-Science, Inc., (ES) undertook the comprehensive RI of Landfills 8 and 10 in the beginning of December 1990. Work was performed for the U.S. Air Force under contract to the Department of Energy and managed by Martin Marietta Energy Systems' Hazardous Waste Remedial Actions Program (HAZWRAP). Ambient-air monitoring was a part of the comprehensive RI program. The description of the sampling methods and the discussion of the sampling results, which are presented in this paper, are documented in detail in the draft RI report submitted to WPAFB<sup>1</sup>.

## DESCRIPTION OF AMBIENT-AIR SAMPLING

Nine sampling sites, including one upwind and one collocated group of samplers, were chosen on and around landfills during each round of sampling. Locations of sampling sites varied for each round based on the wind direction (see Figure 2). The wind direction during Round 1 and Round 5 was predominantly out of the southwest and during the remaining three rounds it was out of the northeast. The upwind sampling site was located in the open area across from the Officer's Club Annex Building 189 for Rounds 1 and 5, and during Rounds 2, 3, and 4 it was placed near the Twin Base Golf Course clubhouse. The three downwind sampling sites (Sites 2, 3, and 4) were located on Landfill 8 during all five rounds. The first of the three sites (Site 3) was placed in what was determined to be the center of the downwind boundary of the landfill. The remaining two sites were located approximately 45 degrees northeast and 45 degrees southwest of the central site. One sampling site (Site 8) was located in the open space of the residential area between Landfills 8 and 10. Three downwind sampling sites (Sites 4, 5, and 6) were placed on Landfill 10 using logic similar to that used for locating sampling sites on Landfill 8. The remaining sampling site (Site 9) was collocated with Site 6 on Landfill 10 in Rounds 1, 4, and 5, and with Site 3 on Landfill 8 for Rounds 2 and 3. The downwind sampling sites of both landfills were moved from round to round so that the samplers were exposed to air after it had traveled across the landfill.

The ambient-air sampling program also consisted of the measurement of several meteorological parameters. Due to the complex terrain of Landfills 8 and 10, one meteorological station was located on each landfill (Figure 2). The key parameters measured were wind direction, ambient temperature, barometric pressure, and precipitation. Wind direction was used to locate sampling sites, temperature and pressure were used to correct the measured

sample volume to standard conditions, and precipitation was used to determine when to start or stop the sampling process. Ambient-air sampling was preceded by at least 24 hours without precipitation, and sampling was stopped when the rainfall exceeded the measurable quantity of 0.01 inches during sampling. Meteorological data were collected concurrent with ambient-air sampling during each sampling round.

Particulate matter below 10 microns (PM-10), 26 VOCs, 32 SVOCs, and 15 metals were measured at each sampling site in each round of sampling. The parameters were selected based on the historical documentation on landfill progression and the results of previous investigations. Maximum concentrations of the detected contaminants at each sampling site during the five rounds of sampling are given in Table 1.

#### Volatile Organic Compounds

The Model 911A portable canister sampler, manufactured by Xontech, Inc., Van Nuys, California, was used for collecting VOC samples.

Sampling of VOCs including methane and certain reduced sulfur compounds was performed by pumping controlled amounts of ambient air into a pre-evacuated 6-liter stainless steel canister. The interior surfaces of the canister were treated using a special method known as SUMMA passivation, in which pure chrome nickel oxide is formed on the inside wall of the canister. The inlet of the sampler was placed approximately 2 meters above the ground surface and about 10 liters of ambient air was collected in each canister over a period of 24 hours. At the end of the sampling event, valves on each canister were closed, an identification tag was attached, and the canisters were shipped by an overnight carrier to the laboratory for analysis.

As sampling of reduced sulfur compounds and ketones in a SUMMA canister has not been well established, stability studies were performed by the laboratory for the three reduced sulfur compounds (hydrogen sulfide, carbon disulfide, and dimethyl sulfide) and three ketones (acetone, butanone, and 4-methyl-2-pentanone). The purpose of this study was to determine whether these six compounds, which are among the 26 VOCs selected, are stable in SUMMA canisters beyond the 24-hour sampling period. Except for hydrogen sulfide, the remaining five compounds were fairly stable. Therefore, hydrogen sulfide was sampled by a field instrument, the Jerome 631 Gold Film Analyzer, capable of measuring from 1 part per billion (ppb) to 50 parts per million (ppm).

#### Semi-volatile Organic Compounds

The Model GPS1 PUF sampler, manufactured by General Metal Works, Village of Cleves, Ohio, was used for collecting SVOC samples from ambient air.

SVOCs including polychlorinated biphenyls (PCBs) were sampled with a combination of a quartz filter and adsorbent cartridge and a high volume sampler. The adsorbent cartridge consisted of XAD-2 resin placed between two polyurethane foam (PUF) pieces in a glass module. The quartz filter was used to separate the suspended particulate matter before the air stream was drawn into the adsorbent cartridge. The cartridges were kept refrigerated in their original containers until needed. Approximately 273 cubic meters (m<sup>3</sup>) of air were drawn through the filter and cartridge in a 24-hour sampling period. The air inlet of the sampler was placed approximately 2 meters above the ground surface.

At the conclusion of the 24-hour sampling event, the XAD-PUF cartridges were packed in their respective containers, placed on ice, and shipped by an overnight carrier to the laboratory.

#### Particulate Matter and Metals

The Model G 1200 High Volume PM-10 Sampler was used to sample PM-10 in the ambient air. The particulate matter was also analyzed for the metals. This high-volume sampler is manufactured by General Metal Works, Village of Cleves, Ohio.

The PM-10 was collected on a glass fiber filter with a high-volume electric blower below the filter. Approximately 1,600 m<sup>3</sup> of air was drawn through the filter in a 24-hour period. Similar to VOC and SVOC sampling equipment, the PM-10 sampler inlet was also set about 2 meters above the ground surface.

Following the completion of the sampling event, the fiberglass filters were removed from the samplers, folded in the center, and placed in individual, sealable plastic bags. The plastic bags were then shipped to the laboratory by an overnight carrier. Filters were weighed to calculate the PM-10 concentration and the particulate matter was subsequently analyzed for metals.

## DISCUSSION OF RESULTS

To assess the extent of ambient-air contamination, the following standards were compared with the detected contaminant concentration in each round:

- National Ambient Air Quality Standards (NAAQS) for lead and PM-10;
- Maximum acceptable ground-level concentrations (MAGLCs) calculated based on the OEPA Guidelines for Review of New Sources of Air Toxic Emissions;
- National Institute of Occupational Safety and Health (NIOSH) recommended values for polynuclear aromatic hydrocarbons (PAHs); and
- Lower explosive limit (LEL) for methane.

The NAAQS for lead and PM-10 are 1.5  $\mu\text{g}/\text{m}^3$  (based on quarterly average) and 50  $\mu\text{g}/\text{m}^3$  (based on annual average) or 150  $\mu\text{g}/\text{m}^3$  (based on 24-hour average), respectively. Except for lead, none of the detected contaminants are regulated by NAAQSs.

The MAGLC values are calculated based on the following OEPA procedure:

- Determine if a threshold limit value (TLV) developed by the American Conference of Governmental Industrial Hygienists (ACGIH) exists for the specific contaminant that is emitted from the source.
- Then divide TLV by 70 to adjust the standard from the working population to general public.

The calculated MAGLCs for the detected contaminants are given in Table 1.

The 10-hour time-weighted average for PAHs recommended by NIOSH is 100  $\mu\text{g}/\text{m}^3$ . Among the detected SVOCs, anthracene, fluoranthene, naphthalene, phenanthrene, and pyrene are classified as PAHs.

The LEL of a combustible gas is defined as the lowest concentration of gas that will combust in the presence of an ignition source and air or oxygen. The LEL for methane is  $33 \times 10^6$   $\mu\text{g}/\text{m}^3$  or 50,000 ppm.

### Volatile Organic Compounds

A total of 17 VOCs were detected in the ambient air. Most of the VOCs were found both in upwind and downwind samples. Among 17 VOCs, only benzene and acetone were measured in excess of their respective MAGLCs. Benzene was detected in excess of its MAGLC of 4.3  $\mu\text{g}/\text{m}^3$  in upwind and downwind samples, whereas acetone was found in excess of its MAGLC of 25,429  $\mu\text{g}/\text{m}^3$  at several downwind sites. Acetone was not detected in any upwind samples. Toluene and xylene were frequently found in the same range in upwind and downwind samples. Chlorobenzene and tetrachloroethene (PCE) were each detected once in the upwind sample, and 1,1,2-trichloroethane (1,1,2-TCA) was also detected once at one downwind site. Methane was detected in all samples in all sampling rounds. Relatively higher levels of methane were detected in air samples from downwind sites on the northern portion of Landfill 10. No MAGLC exists for methane. However, the highest detected concentration of methane is less than 0.01 percent of the LEL for methane. The remaining VOCs were detected in a limited number of samples from upwind and downwind sites.

### Semi-volatile Organic Compounds

Ten SVOCs were detected in the ambient-air samples. Concentrations of detected SVOCs in upwind and downwind samples were generally of the same order of magnitude. Fluoranthene, naphthalene, phenanthrene, pyrene, and 4-methylphenol were found in most of the samples. Except for 4-methylphenol, the remaining four are PAHs. Major sources of PAHs are auto exhaust and emissions from fossil power plants and incinerators. Diethylphthalate and 2-methylphenol were detected less frequently and the remaining three SVOCs were rarely

detected. No NAAQSs exist for SVOCs. However, NIOSH recommends a workplace standard for coal-tar products of 100  $\mu\text{g}/\text{m}^3$  based on a 10-hour time-weighted average. PAHs are the principal components of coal-tar products. The combined concentration of PAHs at each sampling site never exceeded the NIOSH-recommended value. Also, available MAGLCs were used to compare the SVOC concentrations. None of the respective MAGLCs were exceeded.

#### Particulate Matter and Metals

The maximum PM-10 concentration in ambient air at each sampling site was measured in late August 1991. This sampling round was preceded by several days of no rain and high daytime temperatures. However, none of the measured PM-10 concentrations exceeded either the 24-hour NAAQS value of 150  $\mu\text{g}/\text{m}^3$  or the annual value of 50  $\mu\text{g}/\text{m}^3$ .

Ten metals were detected in the ambient-air samples. Concentrations of metals detected in upwind and downwind samples were generally similar. Copper was detected in almost all samples. Arsenic, iron, and manganese were found in more than 50 percent of the samples. Beryllium, lead, mercury, and zinc were detected in a few samples and chromium and antimony were rarely detected. Except for lead, none of the detected metals are regulated by the NAAQSs. The highest detected concentration of lead is more than an order of magnitude smaller than the NAAQS of 1.5  $\mu\text{g}/\text{m}^3$ . For the remaining nine detected metals, MAGLCs were used for comparison. None exceed their respective MAGLCs.

#### CONCLUSIONS

Relatively high levels of methane and acetone were measured at the sampling sites located on both landfills, indicating the possible emission of landfill gases into ambient air through the landfill covers. However, based on the NAAQSs and OEPA guidelines, no ambient-air contamination in the vicinity of Landfills 8 and 10 is evident. Concentrations of most of the detected contaminants in upwind and downwind samples were generally of the same order of magnitude. Benzene was detected in excess of its MAGLC in both upwind and downwind samples. The presence of chlorobenzene, PCE, and benzene in the upwind sample implies the existence of another emission source distinct from the landfills. Chlorobenzene and PCE were not detected in any of the downwind samples.

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2. W.T. Winberry, Jr., N.T. Murphy and R.M. Riggin, Methods for the Determination of Toxic Organic Compounds in Air, EPA Methods; Noyes Data Corporation, Park Ridge, New Jersey, 1990.
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Table 1. Maximum concentration of the contaminants detected during five rounds of ambient air sampling.  
(Results are in µg/m<sup>3</sup>)

Analyte	Site 1 (upwind)	Landfill 8			Landfill 10			Site 8	Site 9 (collocated site)	Calculated MAGLC
		Site 2	Site 3	Site 4	Site 5	Site 6	Site 7			
<b>Metals and Particulate Matter</b>										
Antimony	--- (1)	---	0.0029	---	---	---	---	---	---	7.1
Arsenic	0.0019 J (2)	0.0019 J	0.0019	0.0019 J	0.0026 J	0.0028 J	0.002 J	0.0019 J	0.002 J	2.9
Beryllium	0.0008	---	0.0006	---	---	0.0006	0.0006	0.0008	0.0007	0.03
Chromium	0.0058	0.0061	---	---	---	---	---	---	---	0.7
Copper	0.0259	0.0198	0.0141	0.0143	0.0556	0.0519	0.0370	0.0314	0.0865	2.9
Iron	0.4498	0.2442 J	0.3026 J	0.2934 J	0.2916 J	0.3274 J	0.3142 J	0.1798 J	0.2349	3.3
Mercury	0.0001	---	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.14
Manganese	0.0116	0.0104	0.01	0.0110	0.0097	0.0111	0.0118	0.0085	0.0096	14.3
Lead	0.025	0.0202	0.0163 J	0.0163 J	0.0137	0.0166 J	0.0156 J	0.0182 J	0.0185 J	1.5(3)
Zinc	0.027 J	0.0304 J	0.0275 J	0.030 J	0.0255 J	0.0284 J	0.0295 J	0.0279 J	0.0293 J	71.4
Particulates (PM-10)	43.43	46.42	41.12	45.60	44.74	43.24	45.04	38.29	42.83	
<b>Volatile Organics</b>										
Acetone	---	---	500 N (4)	45,244 J	235,985 J	3,810 J	14,763 J	---	78,582 NJ	25,429
2-Butanone	---	38.73 J	39.62 J	---	---	---	---	---	---	8,429
Benzene	17.3 NJ	16.6 J	---	17.6 NJ	---	7.7 NJ	---	---	---	4.3
Chlorobenzene	3.2 NJ	---	---	---	---	---	---	---	---	657
1,4-Dichlorobenzene	66.3 N	3.00 J	---	---	---	---	---	18.08 J	---	857
cis 1,2-Dichloroethene	---	---	---	---	---	11.92 J	---	---	---	11,329
Ethylbenzene	10.9 NJ	13.06 J	---	---	---	---	11.32 J	---	---	6,200
Methylene chloride	---	---	17.06 J	---	37.96	45.96	25.07 J	---	---	2,486
Toluene	45.2 N	49.0 N	16.2 J	9.82 J	12.1 NJ	12.4 N	21.16 J	18.89 N	10.58 J	2,100
1,1,2-Trichloroethane	---	---	---	53.6 NJ	---	---	---	---	---	786
Trichloroethene	---	17.3 NJ	---	---	---	20.47 J	---	---	---	3,843
Tetrachloroethene	16.32 J	---	---	---	---	---	---	---	---	4,843
Xylene	25.25 J	46.14	11.32 J	---	10.45 J	9.79	58.77	17.41 J	---	6,200
Carbon disulfide	---	---	12.48 J	3.12 J	43.3 NJ	3.12 J	68.64	---	---	443
Dimethyl sulfide	---	---	5.09 J	---	---	5.07 J	4.33 J	2.88 J	---	NA(5)
Hydrogen sulfide	1.4	1.4	1.4	1.8	1.4	1.5	1.6	1.4	1.5	200
Methane	1,184 J	1,381 J	1,184 J	1,578 J	1,776 J	2,302 J	3,025 J	1,250 J	2,433 J	NA

Table 1. Continued

Analyte	Site 1 (upwind)	Landfill 8			Landfill 10			Site 8	Site 9 (collocated site)	Calculated MAGLC
		Site 2	Site 3	Site 4	Site 5	Site 6	Site 7			
Semi-volatile Organics										
Anthracene	---	---	---	---	---	---	---	---	0.0125 NJ	2.9
Fluoranthene	0.0092 N	0.0026 NJ	0.0031 N	0.0029 N	0.0027 N	0.0034 N	0.0035 N	0.0021 NJ	0.0031 N	2.9
2-Methylphenol	0.0026 N	---	---	---	---	---	1.88 N	0.333N	---	NA
4-Methylphenol	0.0126 N	0.0092 N	0.0093 N	0.0162 N	0.0137 N	0.0096 N	6.800 NJ	1.22 NJ	0.0715 N	314
Naphthalene	0.124 NJ	0.102 N	0.1180 NJ	0.148 NJ	0.148 NJ	0.111 N	0.151 NJ	0.1068 NJ	0.1180 NJ	743
Phenanthrene	0.0332 NJ	0.0142 NJ	0.0170 N	0.0159 N	0.0143 N	0.0199 N	0.0166 N	0.0124 N	0.0167 N	2.9
Pyrene	0.0048 N	---	0.0018 N	0.0022 J	0.0016 NJ	0.0022 N	0.0021 N	0.0014 NJ	0.0019 N	2.9
Benzoic Acid	---	---	---	0.177 NJ	---	---	---	---	---	NA
Diethylphthalate	0.0058 N	0.0047 NJ	---	0.0036 N	---	---	0.0098 NJ	---	0.0061 NJ	71.4
2,4-Dimethylphenol	---	0.0015 NJ	---	---	---	---	---	---	---	NA

1. - - Indicates that the analyte was not detected.
2. J Indicates that the analyte was positively identified, but the value may not be accurate.
3. No MAGLC is calculated for lead. The given value of 1.5 µg/m<sup>3</sup> is the NAAQS based on quarterly average.
4. N Indicates the presence of an analyte for which there is presumptive evidence to make a "tentative identification."
5. NA Indicates that MAGLC was not calculated, since a TLV has not been determined.

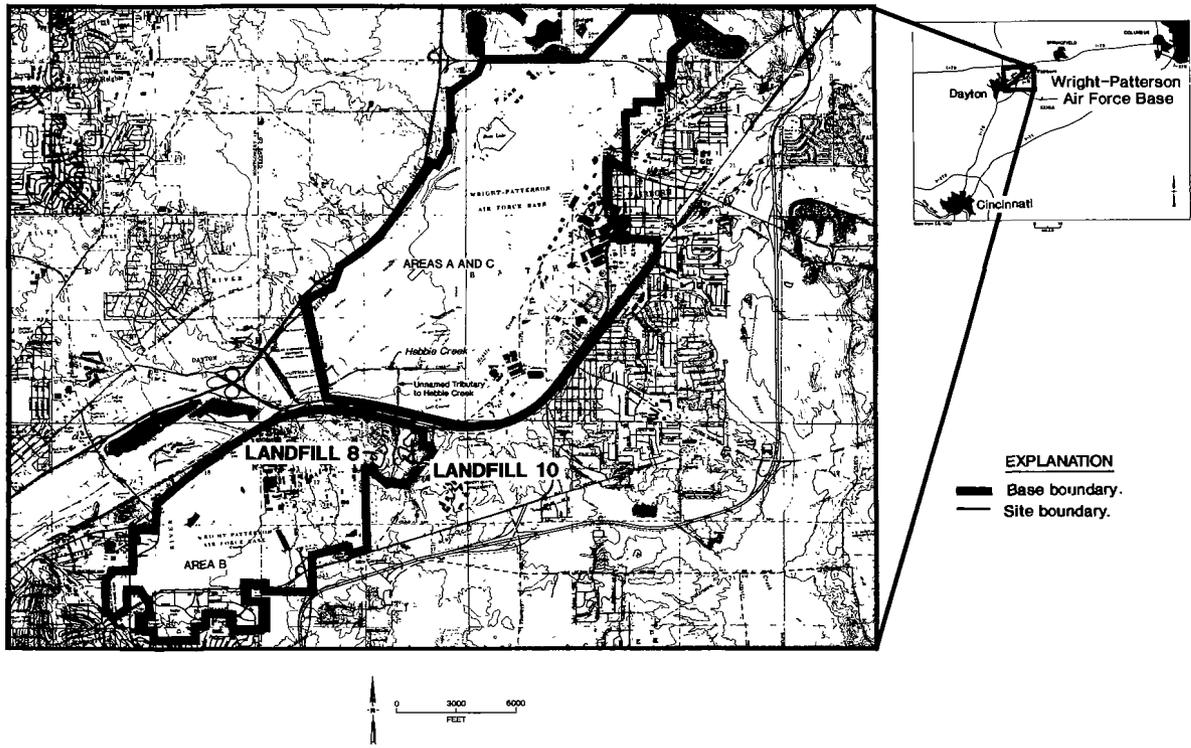


Figure 1. Location of Landfills 8 and 10.

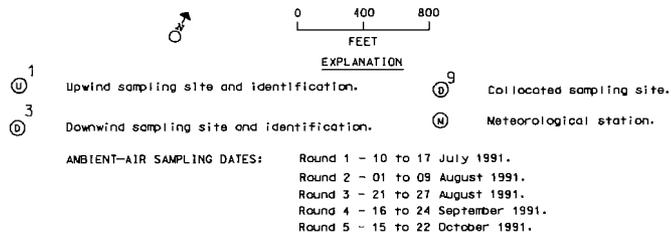
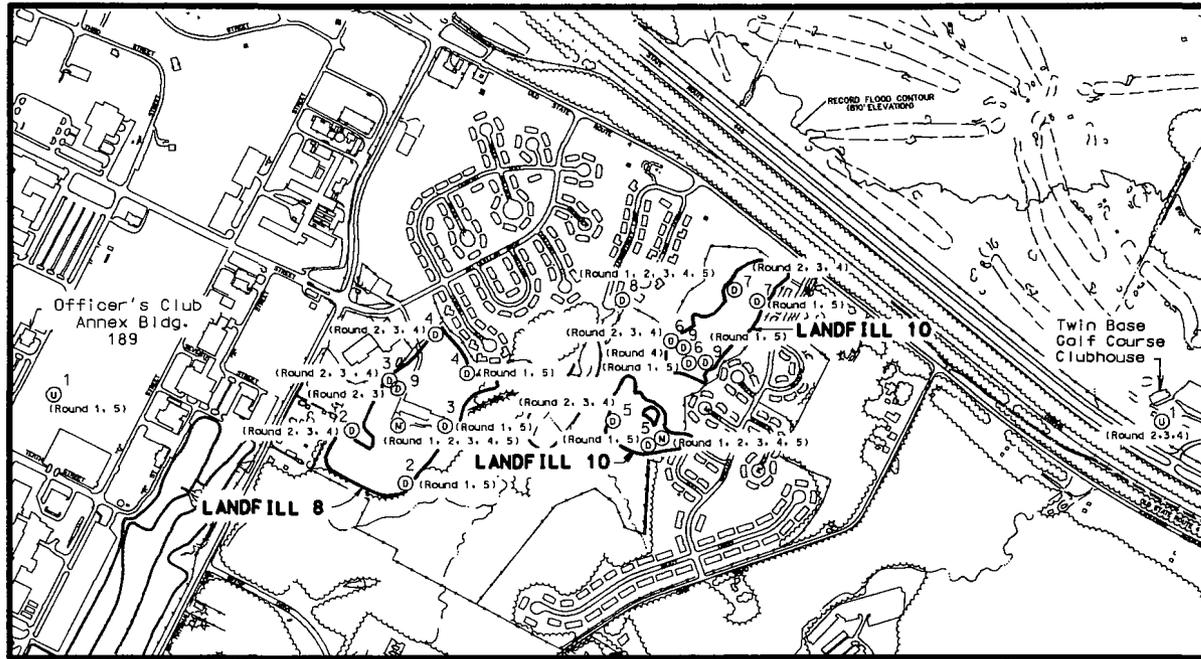


Figure 2. Location of ambient-air sampling sites during five rounds of sampling.

## **The Use of Air Modeling in the Development of the Air Monitoring Program for the Dubose Oil Company Superfund Site Remedial Action**

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Air modeling was used to aid in the development of the ambient air monitoring program at the Dubose Oil Products Company (DOPC) Site. During the remedial action, ambient air monitoring will be performed in order to document that contaminant emissions are not in excess of health-based criteria.

The DOPC Site occupies approximately 20 acres of land in Escambia County, Florida. The site was operated as a storage, treatment, and recycling facility from January 1979 to November 1981. The remedial investigation identified volatile organics, metals, polynuclear aromatic hydrocarbons and pentachlorophenol as contaminants of concern. The remedial action at the site will consist of contaminated soil excavation and on-site treatment by composting/windrowing.

Site contaminants were ranked based on their relative inhalation risks and those posing the greatest threat were selected for air modeling. The emission rates of the selected compounds were estimated and dispersion modeling was performed using the Industrial Source Complex Dispersion Model. The modeling results were used to identify the site contaminants most likely to exceed health based levels during the remedial action and to identify the most appropriate monitoring locations.

This approach may also prove useful in the development of air monitoring programs at other Superfund sites.

### **INTRODUCTION**

#### **Purpose**

Air monitoring is required during the remedial action at Superfund sites to document that site workers and nearby residents are not exposed to site contaminants at concentrations above health based criteria. While ambient air monitoring is necessary to protect public health, the cost of these programs may be significant. The cost of air monitoring is dependent on the following factors:

- number of compounds being monitored;
- number of monitoring locations; and
- frequency of monitoring.

Air modeling was used on this project to identify the most appropriate compounds for inclusion in the air monitoring program and to select the best monitoring locations.

#### **Site Description**

The Dubose Oil Products Company Site occupies approximately 20 acres of land in Escambia County, and is located approximately two miles west of Cantonment, Florida. The site currently consists of an open-sided barn, a soil containment vault, a sump catchment pond, two surface water ponds and an area where soil was excavated before being placed in the containment vault.

The DOPC site was operated from January 1979 to November 1981 as a storage, treatment and recycling facility for handling waste oils, petroleum refining wastes, wood treatment processing waste, paint wastes, spent solvents, and spent iron/steel pickle liquors. Wastes reportedly were thermally treated and/or phase separated.

An emergency response action was undertaken by Florida Department of Environmental Regulations (FDER) during 1984 and 1985 which consisted of constructing an on-site vault for storing contaminated soils for future treatment.

#### **Site Contaminants**

Analyses of environmental samples collected during the Remedial Investigation indicated that the extent of contamination at the site was limited. Contaminants detected at the site include polynuclear aromatic hydrocarbons, chlorinated and non-chlorinated volatile organics, and pentachlorophenol. Trace metals were not detected in site soils and groundwater at concentrations greater than those of uncontaminated soil and waters. Contaminants were not detected in air samples collected at the site.

The highest levels of contaminants were detected in the soil containment vault. Soil samples collected from the vault indicate that contamination is stratified with the highest concentration of volatile and semivolatile compounds present at 25-30 feet below the top of the vault. Volatile organic concentrations in the vault ranged from 22 to 38,270 µg/kg.

Polynuclear aromatic hydrocarbons were detected at concentrations ranging from 578 to 122,400 µg/kg and pentachlorophenol was detected at concentrations ranging from 58 to 51,000 µg/kg.

### Remedial Action

The remedial action at the Dubose Oil Products Company site will consist of the excavation of soils from the vault and contaminated hot spots and biological treatment of the contaminated soils by composting/windrowing.

### Air Monitoring Objectives

During the remedial action, the potential exists for contaminants to become airborne and be transported through the air to residents on or near the site. Because of the potential for contaminant releases to the air, the decision was made to develop an air monitoring program to identify real-time releases of contaminants and use air samples collected for off-site analysis to document air quality at the site.

### AIR MODELING PROGRAM

Air modeling was used to estimate expected contaminant concentrations around the site during the remedial action. These estimated airborne contaminant concentrations were then used to assess the potential health impacts to nearby residents and to select monitoring locations, target analytes, and monitoring frequency.

### Selection of Site Contaminants For Modeling

The inclusion of all site contaminants in the air modeling study would have significantly increased the project cost and extended the schedule. The potential airborne hazard posed by a site contaminant depends upon its potential for airborne release (i.e., volatility), toxicity, and concentration on site. A methodology was developed to select contaminants for inclusion into the modeling program based on their potential inhalation risks. The approach differed slightly for volatile and non-volatile compounds as described below.

#### Volatile Compounds

The most important release mechanism for volatiles is vaporization. A Vapor Hazard Index can be calculated as an indicator of the *relative* hazard posed by specific site contaminants. The Vapor Hazard Index is calculated (for a given chemical) by multiplying the highest concentration found on site by the vapor pressure of that chemical and dividing by the OSHA Permissible Exposure Limit (PEL) for that chemical compound. By definition a PEL for a specific chemical compound is that airborne concentration below which it is believed that nearly all workers may be repeatedly exposed without adverse health affects. The calculated vapor hazard index values for site contaminants were then used to rank the volatile compounds by their relative hazard (i.e., from volatile compounds presenting the greatest relative hazard to compounds presenting the least hazard).

#### Semivolatile and Nonvolatile Compounds

These compounds are released from site soils and wastes primarily due to disturbances of site soils and wastes that may occur during waste excavation, handling, transport and remediation. For screening purposes, the two factors which should be considered when evaluating the inhalation hazard of these compounds are concentrations in site soils/wastes and inhalation toxicity. A hazard index was also calculated for these compounds by dividing the PEL for the compound into its maximum on-site concentration. The *relative* hazard index ranking of these compounds was also used to select specific compounds for subsequent air modeling.

### Contaminant Selection Procedure

Based on the relative inhalation hazard indices calculated for site contaminants, five volatile, ten semivolatile and five metals were chosen for inclusion in the air modeling evaluation. The selected site contaminants were as follows:

- **Volatile Organic Compounds** benzene, methylene chloride, trichloroethene, toluene, and xylene.
- **Semivolatile/Nonvolatile Compounds** benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, chrysene, pentachlorophenol, anthracene, fluoranthene, fluorene, phenanthrene, and pyrene.
- **Metals** arsenic, beryllium, lead, barium, and vanadium

In general the highest ranking compounds were chosen from each group. However, several exceptions were made. For example, acetone, ethylbenzene, aluminum, and iron were deleted from air modeling due to their low toxicity.

## Air Modeling Approach

Following the selection of the chemicals of concern, air dispersion modeling was performed. This modeling involved a two step process: (1) estimation of air emission rates for the chemicals of concern; and (2) dispersion modeling of estimated emissions to determine airborne concentrations at potential receptor locations.

### Contaminant Emission Estimates

Two different estimated emission rates, emissions caused by volatilization and emissions caused by wind-blown dust, were calculated for each remedial activity at the DOPC site. Four remedial activities were selected to represent the primary sources of air emissions. These four sources are described as follows:

- excavation of the vault;
- loading of soil (onto dump truck from front-end loader);
- unloading of soil ( from dump truck to bioremediation cell); and
- bioremediation.

In order to calculate emission rates from the four sources for the chemicals of concern, a conceptual model was developed to depict the planned remedial activities at the site.

### Dispersion Modeling

The Industrial Source Complex (ISC) Dispersion Model was used to estimate contaminant concentrations at potential receptor locations around the site. The ISC is actually a set of two computer programs: the Industrial Source Complex Short-Term Model (ISCST) and the Industrial Source Complex Long-Term Model (ISCLT). These models were used to calculate contaminant concentrations and deposition values at specified receptor locations for various averaging periods. The ISCST model calculates concentration or deposition values for a variety of averaging periods including 1, 4, 8, 12, and 24 hours as well as 1 year. The ISCLT model calculates average monthly, seasonal (quarterly) and/or annual concentration and deposition values.

In this modeling study, the ISCST model was used to determine contaminant concentrations for an averaging period of 24 hours. For volatiles, only contaminant concentrations due to volatilization were modeled. For semivolatiles, the average concentrations due to volatilization and wind-blown dust from each source were modeled separately and added.

### Meteorological Data

The meteorological data used were obtained from the EPA Scram Bulletin Board for the years 1984 through 1989. Meteorological data were obtained from the nearest stations to the DOPC site. Surface wind data and mixing height data for Pensacola and Appalachicola, Florida, respectively, were used.

### Model Sources

The ISCST model accepts three different source types: point, area, and volume. The area type source was selected to model the four sources during the remedial action. The following surface areas were assumed for each source.

- surface area exposure rate during excavation =  $300 \text{ yd}^2/\text{day}$  ( $250 \text{ m}^2/\text{day}$ );
- surface area of a front-end loader bucket =  $3 \text{ yd}^2$  ( $2.5 \text{ m}^2$ );
- surface area of soil during unloading from a dump truck =  $3 \text{ yd}^2$  ( $2.5 \text{ m}^2$ ); and
- surface area of bioremediation =  $2750 \text{ yd}^2$  ( $2300 \text{ m}^2$ ).

### Source and Receptor Locations

The ISCST model is capable (in a single model run) of estimating average concentration values from multiple sources positioned at different locations. The source locations for the dispersion model were selected based on the site layout developed during the remedial design. Figure 1 shows the source locations. Figure 1 also shows the receptor locations.

To more efficiently conduct the modeling for the 15 chemicals of concern, an approach was used which takes advantage of the linear relationship which exists between source strength and resulting concentration values as well as the linear relationship existing between the emission fluxes of the selected compounds and the four sources. The source ratios were obtained by dividing the emission flux calculated for each source by the emission flux calculated for the bioremediation source. These model ratios were used as the source strengths in the model input instructions and a base emission flux for each compound was defined. In using these ratios as the input source strengths in the ISCST model, the ambient impact estimated for each receptor represents a base receptor impact for each receptor. Thus, the compound-specific impacts at each receptor can be obtained by multiplying the base emission flux (for each compound) by the base receptor impact for each receptor.

The maximum 24-hour concentrations of the contaminants of concern at each receptor location were obtained by first modeling the four sources with respective emission ratios and then multiplying the resulting concentrations by the base emission flux calculated for each chemical of concern.

#### Evaluation of Modeled Receptor Concentrations

Two methods were used to evaluate the air modeled concentrations for the selected site contaminants. First, the inhalation risks for carcinogenic and noncarcinogenic site contaminants were assessed using the USEPA risk assessment methodology [1, 2].

The USEPA considers carcinogenic risks to be *significant* if the risk exceeds one excess lifetime cancer case per ten thousand exposed. The total carcinogenic risk calculated for air releases from the site during the remedial action was 1.8 excess lifetime cancer cases per one hundred thousand which is within the USEPA acceptable range even for the maximally exposed individual.

Subchronic reference concentration (RfC) values were used to evaluate noncarcinogenic effects because the remedial action is expected to have a duration of 3 years. To assess the overall potential for noncarcinogenic effects associated with exposure to multiple chemicals, a hazard index approach has been developed by EPA [1]. Ratios of intake:RfC are calculated for each chemical and summed as a hazard index. If the hazard index exceeds 1, it is likely that adverse health effects will occur. The hazard quotients and hazard index for the predicted airborne concentrations of noncarcinogenic site contaminants are considerably less than 1 (i.e., hazard index = 0.007). Therefore, a health risk due to inhalation of noncarcinogenic site contaminants is not indicated.

The second method used to evaluate the model results is based on the Florida Department of Environmental Regulation (FDER) Draft Air Toxics Permitting Strategy which is described in Chapter 403 of the State Regulations. This criterion is based on the OSHA permissible exposure limit (PEL) for each compound as follows:

$$\text{Criteria for Public Exposure} = (\text{PEL}/100) \times (8/24) \times (5/7)$$

The factor of 100 provides a safety factor to protect individuals in the population that are more susceptible than "healthy" individuals. The remaining factors are used to adjust the occupations standard (i.e., 8 hours/day and 5 days/week) to the longer exposure periods associated with airborne exposures to the general public (i.e., 24 hours/day, 7 days/week).

Table 1 presents a summary of the maximum carcinogenic risks, the hazard index, and PEL/420 index for modeled air releases from the site. As shown in Table 1, the concentration of pentachlorophenol is predicted to exceed its PEL/420.

#### Air Monitoring Program

Based on the results of the air modeling study it was concluded that the airborne concentrations of site contaminants should not result in unacceptable exposures at the receptor locations. The model results, therefore, supported the development of an air monitoring program that consists of two components; real-time monitoring with portable instruments and limited air sampling for off-site analysis.

Real-time monitoring will be performed utilizing HNu@s and MINIRAM@s to measure the concentrations of photoionizable hydrocarbons and particulates, respectively. The results of the portable monitoring will be used to implement work practice changes and to trigger additional portable monitoring as well as sample collection for off-site analysis.

Samples will be collected from three locations around the site on a regular basis for off-site analysis for volatile organics and semivolatile organics by methods TO14 and TO13 respectively. The sampling locations are shown on Figure 1. The sampling locations were selected based on the prevailing wind directions the modeling results and the locations of potential receptors. The frequency of sample collection for off-site analysis is dependent on the work activity as well as the results of the portable monitoring. If photoionizable hydrocarbons and particulates are not detected above background levels, samples for off-site analysis will be collected as follows:

- twice per week during the first week of excavation into the vault;
- twice per week during the excavation of the lower vault soils (greater than 20 feet); and
- monthly during the remainder of the remedial action.

Based on the air monitoring results, the frequency of air sampling may be revised.

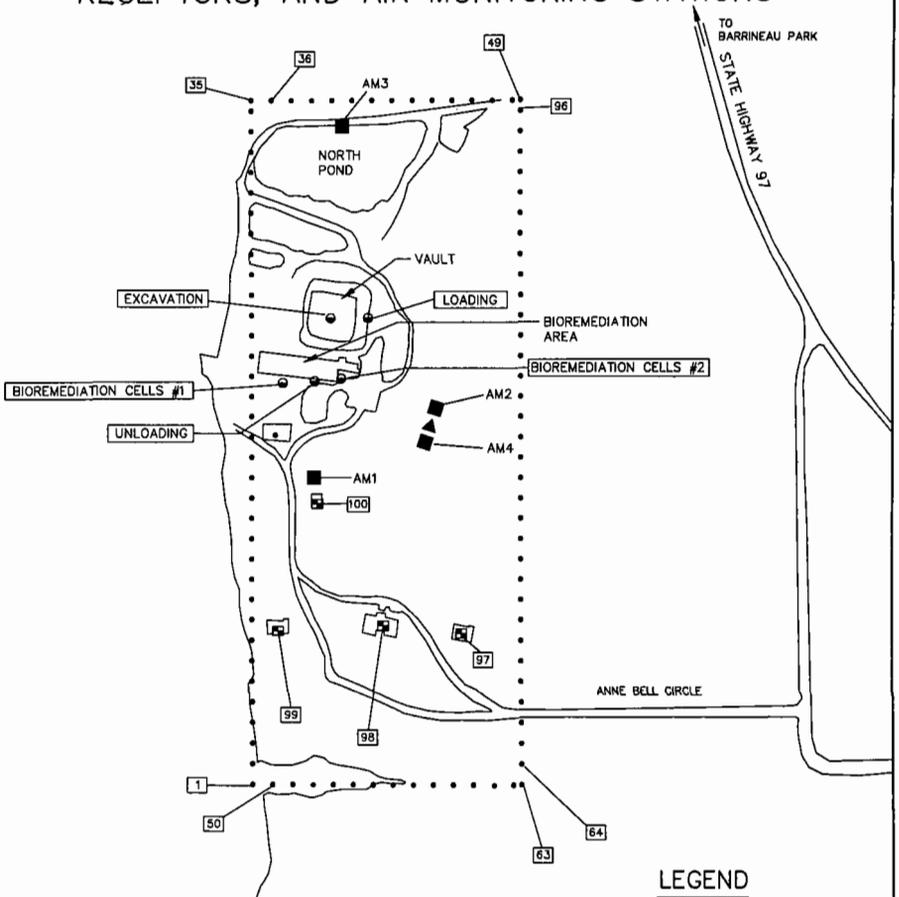
#### CONCLUSIONS

Air modeling was used to aid in the development of the air monitoring program for the Dubose Oil Products Company Site Remedial Action. The air modeling results were used to support a limited air monitoring program and to aid in the selection of target compounds and monitoring locations.

#### REFERENCES

- [1] Risk Assessment Guidance for Superfund (RAGS), Volume IA, EPA/540/14-89/002.

FIGURE 1  
 LOCATIONS OF SOURCE AREAS,  
 RECEPTORS, AND AIR MONITORING STATIONS



**LEGEND**

- FENCE LINE RECEPTOR LOCATION
- POTENTIAL ON-SITE RECEPTOR LOCATION
- 97 IDENTIFIES POTENTIAL RECEPTOR
- AIR SAMPLING STATION
- ▲ METEOROLOGICAL TOWER
- CENTROID OF SOURCE AREA

**TABLE 1**  
**Summary of Air Modeling Results**

Chemical	Max. Predicted	Hazard Quotient		Carcinogenic Risk	Exposure Index
	Concentration	Chronic	Subchronic		Conc (air)
	In Air (mg/m <sup>3</sup> )				(mg/kg/day)
<b>Carcinogens</b>					
Benzene	6.9E-04	--	---	2.4E-07	9.0E-02
Methylene Chloride	9.4E-02	--	---	1.6E-05	2.2E-02
Trichloroethene	9.3E-03	--	---	1.9E-06	1.4E-02
Benzo(a)Anthracene	2.3E-06	--	---	1.6E-08	4.8E-03
Benzo(b)Fluoranthene	5.2E-07	--	---	3.6E-09	1.1E-03
Benzo(k)Fluoranthene	5.2E-07	--	---	3.6E-09	1.1E-03
Chrysene	6.5E-07	--	---	4.4E-10	1.4E-03
Pentachlorophenol	9.6E-03	--	---	---	8.0E+00
Arsenic	5.0E-07	--	---	2.9E-07	2.1E-02
Beryllium	8.9E-08	--	---	8.8E-09	1.9E-02
Lead	7.9E-06	--	---	---	6.7E-02
<b>Noncarcinogens</b>					
Toluene	1.7E-02	8.20E-04	8.20E-04		1.9E-02
Xylene	1.9E-02	6.10E-03	6.10E-03		1.9E-02
Anthracene	7.9E-05	--	---		6.6E-04
Fluoranthene	3.1E-03	--	---		2.6E-02
Fluorene	3.0E-03	--	---		2.5E-02
Phenanthrene	8.1E-04	--	---		6.8E-03
Pyrene	2.3E-06	--	---		1.9E-05
Barium	7.5E-06	1.40E-03	1.40E-04		6.2E-03
Vanadium	3.5E-06	--	---		2.9E-02
<b>Hazard Index =</b>		<b>8.3E-03</b>	<b>7.1E-03</b>		
<b>Total Risk =</b>				<b>1.8E-05</b>	

## **Risk Assessment Methods for Exposure to Environmental Substances Found Indoors**

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### **ABSTRACT**

Measures to control possibly hazardous or unwanted substances in public or commercial buildings as well as residences depend heavily on methods by which risk of exposure to such substances are determined. Two major approaches have been used: (1) extrapolation from high to low dose of exposure and (2) epidemiologic studies that determine if there is an elevated risk for exposed individuals, using unexposed individuals as referents. Two important examples are (1) the recent risk assessment of exposure to environmental asbestos fibers (EAF) by the Health Effects Institute - Asbestos Research in conjunction with the U.S. Environmental Protection Agency and (2) lung cancer risk assessment of building occupants exposed to environmental tobacco smoke (ETS), also by the U.S. Environmental Protection Agency. In practise, the extrapolation and epidemiologic approaches appear to result in risk estimates which differ substantially. The risk estimate based on extrapolation is considerably smaller (by one or two magnitudes) than the risk estimates based on epidemiologic studies. Suitability of each method of risk estimate for EAF and ETS (and other possible substances) and reasons for differences between them will be reviewed.

### **INTRODUCTION**

Two major approaches have been used to estimate risks associated with low dose exposure to substances found indoors: (1) **Downward Extrapolation from high to low exposure**. For example, the Health Effects Institute - Asbestos Research (HEI-AR)<sup>1</sup> in conjunction with the U.S. Environmental Protection Agency (EPA) used downward extrapolation for levels of environmental asbestos fibers (EAF) to estimate asbestos disease risk, and (2) **Epidemiologic studies that estimate the relative risk of exposed individuals with respect to unexposed individuals**. For example, the EPA estimated lung cancer and some other risks to environmental tobacco smoke (ETS) by epidemiologic studies of populations classified into more or less exposed groups by some surrogate of exposure<sup>2</sup>.

The HEI-AR method assumes that health effects of low level asbestos exposure can be obtained by linear extrapolation from effects of heavy occupational exposure. In principle, the lifetime excess risk of individuals exposed to a concentration X times lower than the risk of workers heavily exposed to asbestos is taken to be 1/X times the asbestos workers' excess risk.

The EPA estimates lung cancer or other risks for ETS by comparing mortality or morbidity of never smokers exposed to ETS with that of never smokers not so exposed. Exposure is defined by some surrogate which is thought to be related to dose.

## EVALUATION OF THE HEI-AR/EPA LINEAR EXTRAPOLATION

The HEI-AR Report's risk analysis relies on four assumptions which are highly questionable or may be demonstrably untenable in some cases:

1. That the relative risk of asbestos exposure is linearly progressive;
2. That the composition of EAF is equivalent to the composition of asbestos to which workers are exposed during mining or fabricating operations;
3. That any particular concentration of EAF represents equivalent doses for different exposed populations; and
4. That the health effect of all individuals passively exposed to EAF at the given concentration are qualitatively the same as those of healthy workers exposed to the same concentrations.

Is the relative disease risk of asbestos exposure linearly progressive?

Human studies are of workers who mine, mill or handle asbestos and are exposed without exception to high doses. The shape of a dose-response curve for low levels is in many ways difficult to ascertain from human studies, especially for mesothelioma. However, there are some data from animal and human studies that are measured over a sufficient number of dose levels and that suggest a curvilinear rather than linear relationship between asbestos disease risk and exposure.

Malignant mesothelioma can be easily induced following inhalation or intraperitoneal and intrapleural injections of asbestos fibers in various animals<sup>3,4</sup>. Table 17, Chapter 6 of the HEI-AR Report clearly shows a very rapid rise in tumor response to very low doses, reaching an asymptote of approximately 80% tumors in the exposed animal population. (See our Table 1.) Occupational studies may reveal only the higher range of a dose-response curve of which the unobserved portion may be similar.

Seidman et al<sup>5</sup> also present sufficient human data on mesothelioma to demonstrate the increased risk of mesothelioma as a function of dose but the number of dose values are insufficient to establish the shape of a low dose-response function. They have sufficient data on relatively low exposure to plot SMRs for lung cancer and for all asbestos disease as a function of "estimated fiber exposure starting with less than 6 fibers/cc after 5-40 years since onset of exposure" and for "length of time worked", starting with a period of less than six months. The data for lung cancer and asbestos disease by fiber years/cm<sup>3</sup> and by length of time worked resembles in a qualitative way that of animal data for mesothelioma following intraperitoneal injection. Our Figure 1 plots SMRs of asbestos disease and of lung cancer by estimated fiber exposure as calculated by Seidman et al. The downward progression of SMRs with decreasing exposure (measured by estimated fiber years of exposure or by length of time worked) appears linear for heavier exposure but drops off for lesser exposure. These curves clearly show the appropriateness of a curvilinear relationship. If a straight line would be fitted to SMRs for estimated fiber levels, they would result in SMRs greater than 2.5 when exposure to asbestos fibers equals to zero. Whatever weakness estimates of fiber count have, an intercept value along the SMR axis of greater than 2.5 leaves the investigator trapped between the Scylla of positing a curvilinear function, rapidly dropping off to an SMR value of 1.0 when asbestos dose approaches zero and the Charybdis of assuming the existence of one or more confounding factors which masks the true relationship between asbestos exposure and risk. For further discussion see Sterling et al<sup>6</sup>.

EAF is physically not equivalent to fibers in mining, fabricating or insulating.

EAF varies in distribution of fiber size, type and thickness depending on what material is being released into the atmosphere and how the release is taking place. EAF may be mixed with other fibers. In most instances, EAF probably contains additional toxic materials that have adhered to the fibers and add to their toxicity. Moreover, the average fiber count in a particular building may not be a true indication of actual exposure of occupants and may, in fact, mislead.

Identical concentrations of EAF do not give the same dose to different exposed populations.

Exposure of industrial workers and of children, females, sick persons, institutionalized seniors and handicapped persons to the same fiber concentration results in profound differences in delivered dose.

The health effect of involuntary exposure may not be equivalent to that of occupational exposure.

It is unreasonable to expect that the health effects of blue collar workers and those of a wide range of individuals coming into involuntary contact with EAF would be similar for equivalent exposures.

#### THE EPA'S APPROACH USING EPIDEMIOLOGIC STUDIES.

The EPA<sup>2</sup> and NSC/NRC<sup>7</sup> used similar methods to estimate the health effects of passive smoking. However, the EPA Report is the more complete and will be discussed here.

The lung cancer risk for non smokers (or other disease risks) is determined by comparing mortality or morbidity of non smokers (in most instances spouses of smokers) exposed to ETS with that of non smokers not so exposed or less exposed.

Exposure is defined by a surrogate that is thought to be related to dose and usually are obtained by responses to a questionnaire. Surrogates are used to classify exposure levels. For instance, one study defines exposure as "smoking by any member of the household" while another specifies and classifies exposures by "number of cigarettes smoked by husband". Thus, different surrogates of exposure reflect different levels and amounts of exposure.

#### CONSEQUENCES OF THE CHOICE OF RISK ASSESSMENT METHOD.

Risk estimates obtained by downward extrapolation tend to be considerably smaller than risk estimates obtained by epidemiologic studies. The HEI-AR Report estimates by linear extrapolation that these are 4 to 40 premature cancer deaths per million persons exposed to outside ambient asbestos levels. This figure is not only impossible to verify but even to detect an annual increased risk level of 40 per million would take on the order of 200,000 cases and as many controls. Yet elevated risks of individuals involuntarily exposed to EAF can be determined easily from relatively small samples of exposed individuals. For instance, Joubert et al.<sup>8</sup> observed 43 cancer deaths where 25 would have been expected in a sample of 115 decedents who had been involuntarily exposed to asbestos. Even for such a small sample, the probability of finding such an increase in cancer mortality above that expected by chance is less than 0.003.

Differences in lung cancer risk estimates associated with ETS between downward extrapolation from active smoker risk and those derived from epidemiologic (mostly spousal) studies are again large. Estimates of excess numbers of lung cancer deaths among non smokers in the EPA Draft Report based on epidemiologic spousal studies of excess lung cancer range from 3000 to 3700. On the other hand, the number of excess lung cancer death derived from linear downward extrapolation varies between 12 and 354<sup>9,10</sup>.

Thus, risks established by the epidemiologic method is significantly elevated while that established by downward linear extrapolation tends to be small, in fact so small that it cannot be tested by epidemiologic methods.

The low risk levels established by linear downward extrapolation are invalid because health risk associated with EAF is not linearly progressive; EAF is different in composition and toxicity from fiber encountered in mining and milling of asbestos; and neither dose levels nor health effects can be compared between populations involuntarily and occasionally exposed to EAF with those of healthy blue collar workers occupationally exposed to asbestos fibers.

On the other hand, the elevated risk obtained from epidemiologic studies are confounded by socio/economic factors. Households with spouses and children exposed to EAF or ETS differ in a large number of factors, but mainly in exposure to toxic materials related to lower socio/economic status, to toxic materials brought home on hair, skin and clothing of their spouses employed in industry when compared to households where there are no husbands exposed to asbestos or other toxic substances or no smoking husbands or smoking mothers. Moreover, differences in socio/economic class between households with and without asbestos workers or smokers are large, and with it are differences in many health-related factors. This pattern then raises the questions of the extent to which a comparison of household members with greater exposure (to EAF or ETS) or to other toxic substances) to those with less exposure also compares groups that differ with respect to indirect occupational exposure to toxic substance and/or to the associated social class differences in lifestyle and diets and so on that go along with occupational and socio/economic differences.

These considerations are of utmost importance because there is a uniform difference in mortality tied to social class. Regardless of how social class is measured, by income, by occupation or by socio/cultural factors, there is a consistent difference in mortality by which lower socio/economic stratas suffer from a significantly higher mortality than higher socio/economic stratas<sup>11,12,13</sup>

Finally, risks from asbestos exposure determined by the HEI-AR method cannot be compared to risks from ETS exposure determined by the EPA method because the former risk is determined by a method which assures minimal risk value while the latter is determined by a method which assures maximum risk values.

## CONCLUSIONS

Our review reveals the existence of a dilemma. One solution to the dilemma might be to always perform both types of risk analyses. The better alternative would be to use neither method of risk evaluation. Our brief analysis has shown that results of neither method of estimating risk lacks the needed validity for drawing conclusions about risks to health from low doses. Eliminating or at least decreasing as much as possible the risk to low, occasional and involuntarily exposed populations can be accomplished without knowing for certain the exact values of risk to which these populations are actually exposed. For instance, maintenance workers will be warned and instructed to take due caution in removing installed asbestos in the case of repairs and asbestos workers can be trained not to take home asbestos on their clothing, hair and skin. Similarly ETS exposure can be minimized by proper ventilation and proper location of smoking permitted areas at the workplace -- all this can and should be done quite independently of establishing a risk of involuntary exposure at any level. In cases such as EAF or ETS, when environmental exposure is unavoidable, good industrial hygiene practices ought not to depend on risks associated with poor industrial hygiene practices. Also the need for establishing risk levels for exposure to toxic agents in the workplace for populations necessarily exposed to high levels of toxic materials is quite a separate matter. Here regulation of occupational exposure to almost always very high levels of toxic substances require the determination of risks associated with the occupational environment in order to set standards at levels required to protect exposed workers.

## ACKNOWLEDGMENTS

Support for the ETS analysis came in part from several cigarette manufacturers.

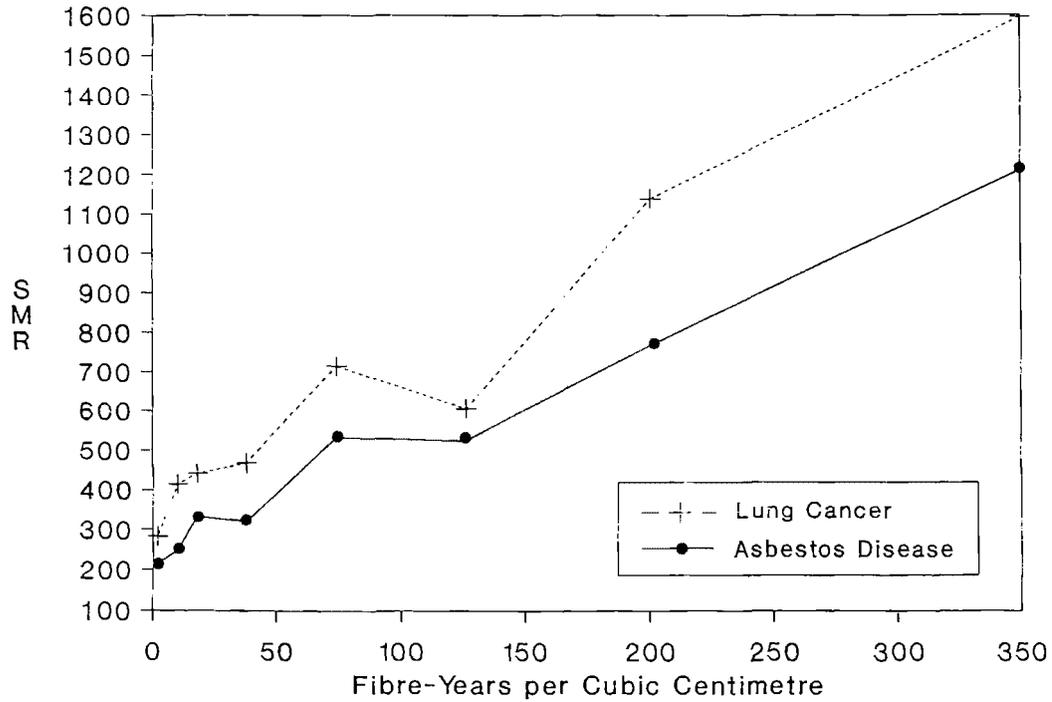
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**TABLE 1. Mesothelioma production in rats in relation to dose from intrapleural and intraperitoneal injection studies. (adapted from the HEI-AR Report, Table 6-17.)**

DOSE (mg)	PERCENT OF TUMORS		
	AMOSITE	CROCIDOLITE	CHRYSOLITE A
15.0	79.2	70.8	79.2
10.0	75.0	41.7	83.3
7.5	62.5	62.5	83.3
5.0	70.8	41.7	79.2
2.5	59.4	56.3	68.8
0.5	46.9	31.3	80.6
0.05	25.0	25.0	37.5
0.01	8.3	0.0	4.3



\*Extracted from Seidman et al, 1986

Figure 1. SMRs of lung cancer and asbestos diseases from 5 to 40 elapsed years since onset of work in an amosite asbestos factory, according to estimated fiber exposure.

## A Pilot Study to Assess Personal Exposures to Ozone in the Fraser Valley of British Columbia

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### ABSTRACT

Personal exposures to ozone were measured in a pilot monitoring study during July and August of 1992. Measurements were made in the Fraser Valley, a suburban and rural river valley bordering the metropolitan region of Vancouver, British Columbia (population approximately 1.3 million). Two groups of 25 healthy individuals were selected for 14 consecutive days of personal monitoring, based on prior expectations of their activity patterns. The first group was composed of adult health care workers who were expected to spend a majority of the work day indoors or commuting. The second group, teenage camp counselors, were expected to spend most of the day outdoors. Time activity data was collected to investigate the association between activity patterns and ozone exposures. Personal monitoring was conducted with the nitrite-coated filter passive ozone sampler. Sampler performance was evaluated and ozone collection rates were determined empirically by collocation of the passive samplers with continuous ozone analyzers for one month at three fixed sites within the region. Inter individual variability of ozone exposures was assessed by comparisons between the camp counselors, who spent the majority of the sampling period in the same general location. Intra-individual variability, as a result of sampler performance, was assessed by collecting a number of duplicate personal samples. Acid aerosols constituents ( $\text{H}^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{NH}_4^+$ ) were also measured for the duration of the study. Although ozone levels were low (< 35 ppb 24-hour average) during the sampling period, the passive ozone sampler agreed well with co-located UV photometric ozone measurements and was found to be feasible for personal sampling. Based on replicate personal samples, personal measurements differing by more than 7 ppb were associated with true differences in exposure. Differences in ozone exposures were observed between the two sampling populations, with higher exposures recorded in the group which spent more time outdoors. Outdoor ozone exposures were estimated to account for 14 - 37 % of the variability in measured personal ozone exposures. Acid aerosols were not detected and aerosol  $\text{SO}_4^{2-}$ -concentrations were low (< 50  $\text{nmol m}^{-3}$ ).

### INTRODUCTION

Recently, concern has been expressed about elevated concentrations of ozone and other constituents of photochemical smog in the Fraser Valley airshed of British Columbia. The Fraser Valley has experienced many of the highest ozone concentrations in Canada, and potential for continued adverse air quality is expected to persist as development in the region continues<sup>1</sup>. While there is a wealth of data regarding concentrations of major air pollutants, including ozone, little is known regarding the distribution of population exposure to these pollutants and the mitigating factors resulting in variable exposures in the resident population. Knowledge of population exposure to ozone will be important in order to assess the effectiveness of future strategies for reducing photochemical oxidant pollution in the Fraser Valley and to provide useful information for the development of new reduction strategies. Among other factors, exposures to ozone are likely to be affected by spatial variability in ambient concentrations, the degree of penetration of ambient ozone into varying indoor environments, characteristics of the indoor environment which affect ozone reactive decay (residence time, surface materials, other reactive pollutant concentrations), the relationship between time-activity patterns of the population and ozone concentrations within specific microenvironments (commuting, workplace, etc.) and the relationship between time-activity patterns of the population and the diurnal ozone concentration profile.

Furthermore, while the health effects of ozone at concentrations experienced in ambient air have been demonstrated repeatedly in clinical chamber studies the epidemiological evidence supporting ozone health effects is less convincing<sup>2,3</sup>. One limitation is the lack of personal exposure data for ozone. These data are limited since conventional ozone monitoring equipment (UV photometry, chemiluminescence) is bulky and expensive. The recent development of an inexpensive and simple passive monitor for ozone provides a new opportunity to examine the distribution of population exposures<sup>4,5</sup>. Perhaps a more significant limitation of previous North American ozone epidemiological studies, particularly those conducted in eastern regions, is the coincidence of ozone episodes with those of acidic sulfate species<sup>6,7</sup>. Human chamber and animal studies suggest that both ozone and acidic aerosols may be associated with adverse respiratory health outcomes, and evidence for potentiation interactions also exists<sup>8,9</sup>. However, from a regulatory and policy viewpoint, control strategies for acidic aerosols and ozone are distinctly different. Although several SO<sub>2</sub> sources (oil refineries, cement plants) do exist in the Vancouver metropolitan area, the lack of major oil or coal-fired sulfur emissions sources in the greater Vancouver area make it unlikely that significant concentrations of acid aerosols will be observed in the Fraser Valley. However, no measurements have been made to date. By demonstrating that ozone episodes occur in the Fraser Valley in the absence of elevated concentration of acid aerosols, the potential confounding effect introduced by acidic aerosols can be reduced eliminated in epidemiological investigations.

## METHODS

**Aerosol Acidity.** Daily ambient aerosol strong acidity monitoring was initiated in mid July 1992 at 3 sites in the Greater Vancouver Regional District (GVRD): Kensington, Pitt Meadows and Chilliwack. A total of 60 valid 24-hour samples were collected at each of the three sites (100% valid sample collection). Samples were collected at a flow rate of 4 L min<sup>-1</sup> with the Harvard Aerosol Impactor / Aluminum Honeycomb Denuder system. Sampler inlets were located 1.5 m above all surfaces and at least 1 m from major supports. Teflon membranes were analyzed for aerosol strong acidity by the method of Koutrakis, et al<sup>10</sup>. Remaining filter extract was analyzed for SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> by ion chromatography (Dionex 2000i). Limits of detection, based on a 24-hour sample collected at a flow rate of 4 L min<sup>-1</sup> are 15, 3.5 and 20 nmoles m<sup>-3</sup> for SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup>, respectively.

**Ozone.** To calculate the sampling rate of the passive ozone sampler, passive ozone samplers were collocated with UV photometric (TECO 49) continuous ozone analyzers at three continuous monitoring sites: Pitt Meadows Abbotsford and Chilliwack. The Chilliwack site was a rural location at the far end of the Fraser Valley from Vancouver (approx. 60 miles from the city center). The Pitt Meadows site was a rural-suburban location about 20 miles east of Vancouver. The Abbotsford site was a suburban site approximately 45 miles east of Vancouver. Due to logistic constraints the passive sampler was suspended near the library entrance (approximately 2m above ground level) while the inlet for the continuous analyzer was on the roof (approximately 4.5m above ground level). All continuous analyzers were calibrated weekly and a full site audit was performed monthly. 24-hour average samples were collected daily for a period commencing in mid July 1992. Passive samplers were placed inside a wind and rain cover which was hung on a tripod placed at least 1 m from all major supports and building faces. Except as noted the sampler inlet was approximately 1.5 m above surface level and as close as feasible to the sampling manifold inlet of the continuous ozone analyzer. Passive samplers were prepared in the laboratory within four days of their deployment in the field. Sampler preparation and analysis procedures are described elsewhere<sup>4,5</sup>.

Personal exposures to ozone were monitored in two population groups residing in the Fraser Valley. Personal samples were collected by clipping the sampler onto their (normal) clothing in the breathing zone. Samplers were worn continuously for 24-hours, except while sleeping or bathing, during which time the sampler was placed (still exposed to air) near the individual. A group of 25 individuals working at a medical clinic in Abbotsford (LFV) were selected to wear passive ozone samplers daily during a 14-day period. From this group, a total of 320 valid samples were collected. Hourly time-activity data, recorded by self-administered logs, were completed for each valid sample obtained. Ozone exposures were also measured in a group of 25 individuals (during a separate two-week period) selected from the staff of an overnight camp (CLU) located across the Fraser River from Abbotsford. These individuals were expected to have different activity patterns than the LFV population group, as the majority of their day was spent outside or in cabins at the camp site. An identical sampling protocol was followed by this group. A total of 289 valid personal ozone samples were collected from the CLU group. During the period of personal ozone exposure monitoring, each group of 25 individuals also provided twice daily measurements of peak

expiratory flow with Mini-Wright peak flow meters. These measurements were self-administered, following an orientation, and daily checks with the field technician.

## RESULTS AND DISCUSSION

No aerosol strong acidity was detected on any of the samples (LOD = 10 nmoles m<sup>-3</sup>). Anion and cation measurements were also low and the results will not be discussed further in this manuscript. Maximum concentrations of SO<sub>4</sub><sup>2-</sup> were below 50 nmol m<sup>-3</sup> (mean: 18 nmol m<sup>-3</sup>) while the maximum concentrations of NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> were below 35 (mean: 4.5) and 100 (mean: 30) nmol m<sup>-3</sup>, respectively.

**Passive Monitor Sampling Rate.** For calculation of the passive sampler sampling rate, data from co-located passive samplers were compared to data obtained from continuous analyzers (TECO 49) at three sites. Sampling rates for the passive samplers were determined by goodness of fit for a linear relationship between the passive and continuous measurements at Pitt Meadows and Chilliwack. The Abbotsford site was excluded from the determination of the overall sampling rate as the relationship between the passive and continuous measurements was much weaker than at the other two sites and differed significantly from those previously reported<sup>4,5,11</sup>. The slopes determined for the Chilliwack and Pitt Meadows sites were in good agreement with each other and with those previously reported<sup>4,5,11</sup>. The average of the slopes from these two sites was then used as the overall sampling rate for all three sites as well as all personal samples (25.9 cc/min). Blank values were subtracted from all samples (mean blank = 1.19 µg concentration in extract). Using the sampling rate of 25.9 cc/min we then compared 24 hour average ozone concentrations from the passive sampler with the mean of the hourly average concentrations from the continuous analyzer at each of the three co-location sites:

**Chilliwack:** Passive = 0.89\*Fixed (r<sup>2</sup> = 0.88; Intercept: non-significant; N=35)  
**Pitt Meadows:** Passive = 0.76\*Fixed + 5.3 ppb (r<sup>2</sup> = 0.69; N=34)  
**Abbotsford:** Passive = 0.40\*Fixed (r<sup>2</sup> = 0.34; Intercept: non-significant; N=34)

Both the Chilliwack and Pitt Meadows sites showed good agreement between the passive and continuous measurements, while agreement at the Abbotsford location was poor as seen by the low slope and r<sup>2</sup> values. The poor agreement at this site can be explained by the difference in sampler placement. As the passive sampler was located closer to surface level, ozone concentrations at this altitude are expected to be lower as a result of reaction between ozone and surfaces. Additionally, as this site was the most urban of the three co-location sites, ozone reactions with NO from auto exhaust are expected to have reduced surface level ozone concentrations further. This measurable difference between ozone concentrations at near surface level elevations differing by only 2.5m supports continued personal or microenvironmental measurements of ozone exposures as monitoring network measurements collected at heights greater than breathing zone heights will tend to be positively biased with respect to human exposure.

**Quality Control.** Initial evaluation for differences in blank values from different filter coating batches or field placements, indicated that blank variation was random. Accordingly, all field blanks (N=53) were pooled together and an overall blank value was used for correction of sample values (Table 1). Lab blanks (N=15) were not significantly different from field blanks, indicating that there were no exceptional problems in the field sampling procedures. All of the blank response was explained by the laboratory portions of the method itself (filter preparation extraction and analysis). The limit of detection (LOD) of the passive sampler method was calculated to be 8.1 ppb, based on 3\*standard deviation of the field blanks. This LOD is in good agreement with those reported previously<sup>4,5,11</sup>.

**Table 1. Personal Ozone Samples Quality Control Parameters.**

Parameter	N	Mean	S.D.	Range
Field Blank	53	12.5	2.7	6.4 - 18.5
Lab Blank	15	13.9	1.7	10.4 - 17.2
Duplicates (difference)	12	3.0	2.1	0.5 - 7.6

Additionally, a series of duplicate personal ozone samples were collected and analyzed. Subjects were instructed to wear one sampler on the right side of the chest and one on the left side for identical sampling durations. All duplicate samples were analyzed during the same sampling run. After subtracting the global blank value from each of the duplicate samples we calculated the difference in the resulting ozone concentration (ppb) between the two samples. The mean, standard deviation and range of these differences are reported in Table 1. Using a value of  $1.96 \times$  the standard deviation of the differences, we can estimate that 95% of random differences between two personal exposure measurements will be less than 7.2 ppb. Therefore, with these confidence limits any two personal exposure samples differing by less than 7.2 ppb (assuming a 24-hour sampling duration) cannot be considered to be a true difference in personal exposure. Although no replicate results for the passive sampler have been reported to date, Liu, et al<sup>11</sup> estimate the relative error of the method to be 15-25%. Consequently, a 50 ppb sample would have a relative error of 7.5 - 12.5 ppb. Given the low ozone concentrations during the sampling period and the estimated method error, our calculation of a 7.2 ppb 95% confidence interval for differences in replicate personal measurements suggests that no additional error was introduced by collecting personal samples.

Comparisons between the personal ozone samples and fixed-location monitors (continuous at LFV and fixed-passive monitor at CLU) are shown in Figures 1 and 2. Although ozone concentrations were quite low during the duration of the monitoring and many measurements were below the LOD, we still observed variability in personal exposures, beyond that which could be explained by the variability in the method itself. With only a few exceptions, personal exposures were lower than fixed location monitors, although mean personal exposures generally tracked along with the fixed-location monitor concentration. The mean differences between continuous ozone and all personal ozone measurements were 12 and 8.5 ppb for LFV and CLU, respectively. Time-activity data indicated that the two groups differed significantly in the amount of time spent outdoors. The mean percentage of time spent indoors, outdoors and in transit were 84.8, 9 and 5.5%, respectively for the LFV group. The CLU group spent, on average, 72.4, 25.8 and 1.9% of time indoors, outdoors and commuting, respectively. Since we found significant differences between the time-activity patterns of the two groups, we used the time-activity data to predict differences in personal exposures. Exposures estimated from time-activity data and fixed-location monitors (fraction of time outdoors  $\times$  outdoor concentration) and measured personal exposures showed the following relationships.

$$\text{LFV: Estimated Personal Exposure} = \text{Measured Personal Exposure} \times 0.27 \text{ (non-significant intercept)}$$

$$r^2 = 0.37 \quad N = 232$$

$$\text{CLU: Estimated Personal Exposure} = \text{Measured Personal Exposure} \times 0.19 + 2.79 \text{ ppb}$$

$$r^2 = 0.14 \quad N = 251$$

The relationship between the measured and estimated personal exposures can be compared with that described by Liu, et al. for the measurements in State College, PA for 81 samples<sup>11</sup>. These investigators found an overall model  $r^2$  of 0.33 with a coefficient for estimated personal exposures (based on outdoor concentration and time only) of 0.52. The coefficient for indoor concentration and time was significantly higher (0.82), indicating the importance of indoor exposures in determining the total personal exposure. In light of the results of Liu, et al., our estimated exposures based only on outdoor concentration and time show that exposures of different population groups can be predicted to varying degrees by the amount of time spent outdoors. For these data, although the personal measurements for the CLU population were closer to the fixed-location measurements (Mean ratios of personal: fixed location ozone were 0.53 and 0.35 for CLU and LFV, respectively), the fixed location measurements and the time spent outdoors explained less of the variability in personal exposures. This is likely due to the higher indoor ozone concentrations experienced by this group. When indoors, these individuals were primarily in wood cabins with open windows, structures which would be expected to yield elevated indoor:outdoor ozone concentration ratios. In contrast the LFV population, when indoors, were primarily in mechanically ventilated offices or in their homes, both environments would be expected to have lower indoor:outdoor ozone ratios than the cabins at the CLU site. Accordingly, this population's exposure is dominated by outdoor exposure more than the CLU group.

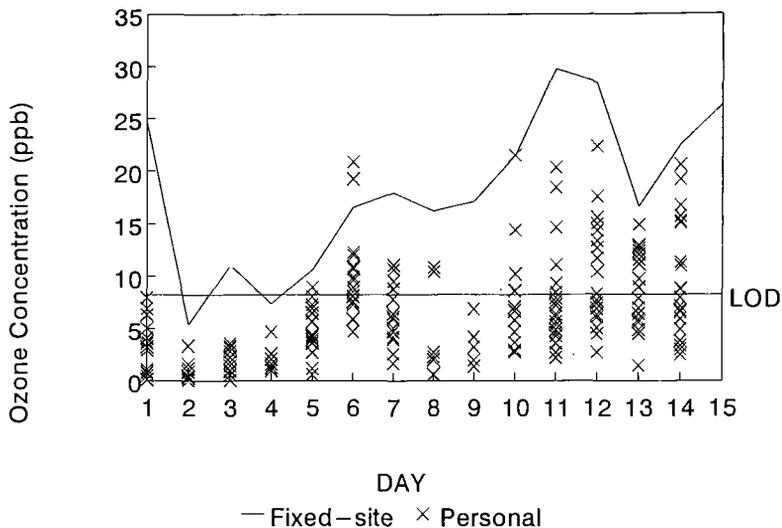
## CONCLUSIONS

Co-location experiments with the passive ozone sampler indicated good agreement with UV photometer continuous analyzers. The positive response of blank samplers was quite consistent and appeared to be a result of coated filter preparation and not contamination during sampler assembly storage or analysis. Duplicate personal samples indicated that no additional measurement error was associated with collecting personal samples although the error inherent in the method suggested that only differences in personal exposures greater than 7.2 ppb could be considered true differences in exposure.

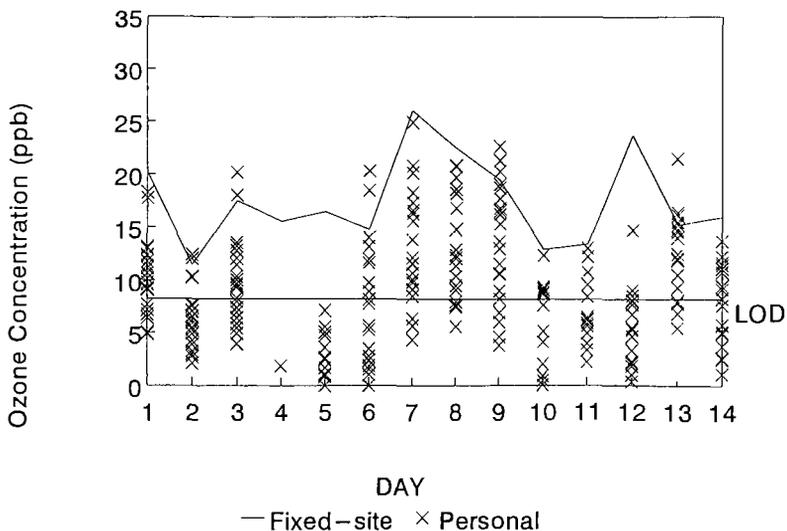
Although ozone concentrations during the sampling period were low, we observed inter individual variability in ozone personal exposures using a passive dosimeter. Measurements in two populations groups who spent different amounts of time outdoors indicated that increased time spent outdoors was associated with increased exposure to ozone, although an improved explanation of the variability in ozone exposures was not associated with time spent outdoors. This observation suggests that variability in ozone exposure is associated with exposure in other microenvironments, particularly indoors. Comparisons between fixed-location continuous monitors which were part of a regional monitoring network and personal monitoring indicated that personal exposures were substantially lower than reported ambient concentrations. One explanation for the overestimation of personal exposures by the fixed-site network was suggested in this pilot study to be the elevation of the continuous monitoring network samplers above the height of the breathing zone. At the height of the breathing zone, ozone concentrations are expected to be lower as a result of reaction with surfaces, resuspended dust and NO from automobile exhaust. Additionally, during this limited monitoring period we observed no measurable aerosol strong acidity and low levels of aerosol  $\text{SO}_4^{2-}$ , indicating that epidemiological investigations of effects of ozone exposure on respiratory health conducted in the Fraser Valley are unlikely to suffer from confounding by acid aerosols.

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**Figure 1.** Relationship between fixed location (continuous analyzer average) and measured personal exposure samples for LFV study population. Each X denotes an individual sample. Personal exposure sample concentrations were corrected for concentration of field blanks and therefore only samples where resulting concentration was > 0 are shown. Horizontal line denotes limit of detection of 8.1 ppb for 24 hour sample.



**Figure 2.** Relationship between fixed location (fixed location passive sampler located at CLU site) and measured personal exposure samples for CLU study population. Each X denotes an individual sample. Personal exposure sample concentrations were corrected for concentration of field blanks and therefore only samples where resulting concentration was > 0 are shown. Horizontal line denotes limit of detection of 8.1 ppb for 24 hour sample.

***Session 13***

***Mercury in the Environment***

## MERCURY DETERMINATION IN ENVIRONMENTAL MATERIALS: METHODOLOGY FOR INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS

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Air particulate samples have been collected at five sites across Upstate New York since October 1991. Automatic dichotomous samplers with a PM-10 inlet were used to collect fine particles ( $< 2.5\mu\text{m}$ ) and coarse particles (2.5 to  $10\mu\text{m}$ ). Vapor phase mercury has also been collected on charcoal sorbants at the same sites.

Samples were analyzed for their trace element content by instrumental neutron activation analysis, INAA. In general the determination of mercury in environmental samples is done by irradiating the sample with neutrons, followed by a radiochemical separation of mercury and subsequent detection of the 279.2 keV gamma ray from Hg-203. This is tedious work if one analyzes many samples. At MIT, we have found the isotope Hg-197 to be better suited for INAA based on its decay properties and the absence of any required radiochemical separation.

If the Hg-203 isotope is used in INAA for determination in unknown matrices which may contain both Ta and Se, the situation is rather complex. The 279.2 keV line used for Hg-203 determination can not be separated from 279.5 keV line of Se-75. By knowing the branching ratios in the decay of Se-75, we can determine the amount of 279.5 keV radiation by measuring the 264.6 keV line of Se-75. Yet this line is not unique as it has interference from 264.1 keV gamma ray of Ta-182, and this should be corrected through 1221.0 keV line of Ta-182. The three-stage correction introduces errors due to simple subtractions and uncertainties in branching ratios and detector efficiencies.

Therefore we used 77.4 keV line from Hg-197 instead of Hg-203 to measure total mercury. It provides a more sensitive measurement because of its much higher production cross section and its shorter half-life. We have successfully applied this approach to hundreds of environmental samples and verified the suitability of this methodology.

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## Introduction

Mercury is an element of significant toxicologic importance which may cause well-characterized health problems in humans. As a result, mercury emissions from anthropogenic sources have become a major environmental issue. In addition to natural sources of mercury, fossil fuel combustion, waste incineration, and smelters also add this element to the environment<sup>1</sup>. Because of its high vapor pressure, mercury is emitted to the atmosphere primarily as a vapor, as opposed to the aerosol form, and it persists in this physical state. The tendency in its natural state to volatilize and its toxicity both as a vapor and when incorporated in organometallic compounds have been long recognized<sup>1</sup>.

In the past a large number of analytical techniques have been applied to determine the Hg content of a variety of environmental samples<sup>2,3</sup>. Among those utilized have been UV absorption spectrophotometry, atomic emission spectrometry, thin gold-film surface resistance, Instrumental Neutron Activation Analysis (INAA), Radiochemical Neutron Activation Analysis (RNAA), and X-Ray Fluorescence (XRF). In general many of these methods depend upon preconcentrations of the mercury in some medium with a subsequent and immediate release of the mercury into a detecting device. Each of these methods has various advantages and disadvantages<sup>3</sup>.

Instrumental neutron activation analysis is one of the most sensitive, selective, and reliable techniques available for the determination of trace elements. It is non-destructive and capable of detecting up to forty elements at small concentrations.

## Assessment of Mercury Determination by INAA

In general the determination of mercury in environmental samples is accomplished by irradiating the sample with neutrons, followed by a radiochemical separation of mercury and subsequent detection of the radiation characteristic of a particular mercury isotope. Usually the 279.2 keV gamma ray from Hg-203 is the detected radiation. At MIT we have found the isotope Hg-197 to be better suited for instrumental neutron activation analysis based on its decay properties and the absence of any required radiochemical separation.

As seen in Table 1, two naturally occurring mercury isotopes are suitable for total Hg determinations, Hg-196 and Hg-202. Although Hg-196 has a lower abundance compared with Hg-202, Hg-196 is much more sensitive for total Hg determinations. This is mainly due to its higher cross section and shorter half life. Under identical irradiation conditions, e.g. 12h irradiation with a thermal neutrons, Hg-197 production is 50 times larger than Hg-203. Additionally, the 77.4 keV gamma line of Hg-197 is free from interference of other radiation, while the 279.2 keV gamma line from Hg-203 is not.

If the Hg-203 isotope is used for determinations in unknown matrices which may contain both Ta and Se, the situation is rather more complex. The only line that is used in Hg-203 determinations is at 279.2 keV, which can not be separated from 279.5 keV line of Se-75. In order to know how much of the radiation measured at "279.2 keV" is from the 279.2 keV line of Hg-203 alone, we must subtract from the measured intensity the contribution from the 279.5 keV line of Se-75. By knowing the branching ratios in the decay of Se-75 we can determine the amount of 279.5 keV radiation and the needed correction by measuring the 264.6 keV line of Se-75. Yet this line also is not "unique" as it has interference from the 264.1 keV gamma ray of Ta-182. However the contribution of this Ta radiation can be corrected for by measurement of the 1189.0 or 1221.0 keV lines of Ta-182 which are not interfered with by any other radiation. If we measure total areas under 279, 264 and 1221 keV gamma ray peaks determined with a HPGe detector the above correction can be made by using the following equation:

$$279(\text{Hg}) = 279(\text{Total}) - 0.42 [264(\text{Total}) - 0.57 \times 1221(\text{Ta})] \quad (1)$$

where 279(Hg) and 1221(Ta) are the areas under the peak as at 279 keV and 1221 keV corresponding to Hg-203 and Ta-182 respectively. The 279(Total) and 264(Total) are the total areas under the gamma ray peaks at 279 and 264 keV. The coefficients are calculated taking into account gamma ray intensities given in Table 1 and relative detector efficiencies of gamma rays involved. For this calculation the ratios of efficiency are taken as

$$\frac{\text{Eff (279)}}{\text{Eff (264)}} \cong 1 \text{ and } \frac{\text{Eff (264)}}{\text{Eff (1221)}} \cong 4.3.$$

This three stage correction introduces errors due to the simple subtraction and uncertainties in branching ratios and detector efficiencies. Depending upon the relative concentrations of Hg, Se and Ta in the sample, it may not be possible occasionally to determine Hg and/or Se with an acceptable accuracy.

Therefore, we prefer to use the 77.4 keV line from Hg-197 in our experiments to determine total mercury as, unlike Hg-203, it is free from other interfering lines and their concomitant corrections. We can still utilize Hg-203 for internal quality assurance whenever it is observed.

## Experiments, Results and Discussion

We have been collecting air particulate samples from five sites across Upstate New York since October 1991. Samples have been collected for 24 hour intervals for a period of two years. The sites are maintained and the collectors changed weekly by the New York Department of Environmental Conservation (NYDEC) and the Adirondack Lakes Survey Corporation (ALSC) personnel<sup>4</sup>. Automatic dichotomous samplers with a PM-10 inlet are used to collect fine particles (< 2.5 μm) and coarse particles (2.5 to 10 μm). During the 2-year study, 7300 samples (3650 fine and 3650 coarse) will be collected. We have also analyzed vapor-phase mercury collected on charcoal sorbants at these same sites.

Samples were analyzed for their trace element content by instrumental neutron activation analysis<sup>5</sup>. To determine Hg and other elements with long half-lives ( $t_{1/2} > 1$  day), samples were irradiated at the MITR-II Nuclear Reactor for a period of 6-12 hours at a neutron flux of  $8 \times 10^{12}$  n/sec.cm<sup>2</sup>. After 2-3 days of cooling, gamma-ray emission from the samples was measured with a high purity Germanium detector with FWHM of about 1.75 keV for the 1332 keV line of Co-60. For the purpose of this study, we will only present a few Hg, Se and Ta results from fine particles collected at the Moss Lake (ML) and Perch River (PR) sites and one charcoal sample (CH) used for vapor phase mercury collection. In Table 2 we present atmospheric Hg, Se, and Ta concentrations in ng/m<sup>3</sup> in ML and PR samples and also in our charcoal in μg/g. In these calculations 77.4 keV, 264 keV and 1221 keV gamma-ray were used for Hg, Se and Ta determinations, respectively. In Table 3 the areas under the 77, 279, 264 and 1221 keV gamma-ray peaks are given.

If we apply Eq. (1), we obtain corrected 279 keV (Hg) areas, which are given in the last line of Table 3. As seen almost all of the 279 keV intensity comes from Se-75 in the case of ML921217 and charcoal samples. As a result one can not determine Hg using the 279 keV line. Also, for the PR samples, the area under 77 keV Hg-197 line is about five times more intense than the corrected 279 keV Hg-203 line. The 77.4 keV line from Hg-197 is interference-free and in many cases is the only way to determine Hg by instrumental neutron activation analysis.

Unlike most other techniques INAA does not require any sample dissolution, addition of reagents or other pre-analysis sample preparation. Therefore, it is easy also to examine materials that would be very difficult to dissolve, such as charcoal, rock and mineral samples.

With respect to mercury determinations, the main problem is mercury loss during irradiation. Mercury has some distinct characteristics under neutron irradiation. Mercury can readily leave the sample matrix due to several causes: for example, hot atom chemistry, and sample heating in a reactor core. This heating is produced from fission and also (n,p) and (n, α) reactions occurring in the sample matrix if fast

neutrons are significantly present in the beam. To eliminate this problem a common practice is to heat seal samples in clean pure quartz tubes. Following the irradiation, gamma-ray spectra should also be measured with the quartz tubes intact.

At MIT we use an irradiation port for Hg determination which is cooled to room temperature and has a very low fast neutron component. MIT's reactor is unique in these respects. These properties effectively eliminate any loss of mercury due to sample heating and there is no need to encapsulate samples in quartz tubes.

We have successfully applied this approach to hundreds of environmental samples and have verified the suitability of this methodology. Filtered atmospheric particulate material and vapor-phase mercury collected on charcoal sorbants were packaged in vials. After the irradiations, and 2-3 days of cooling, mercury in these samples were determined using 77.4 keV gamma ray from Hg-197. Results of these experiments will be presented elsewhere.

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Table 1. Nuclear Reactions in Hg Determinations

Nuclear Reactions	% Abundance of Stable Isotopes	$\sigma$ (barns)	$t^{1/2}$ (days)	E $\gamma$ of Product Nuclei, keV (% abundance)
$^{196}\text{Hg} (n, \gamma)^{197}\text{Hg}$	0.15	3100	2.672	77.4 (18.2)
$^{202}\text{Hg} (n, \gamma)^{203}\text{Hg}$	29.8	4.9	46.61	279.2 (77.3)
Interfering reactions				
$^{74}\text{Se} (n, \gamma)^{75}\text{Se}$	0.9	52	119.8	279.5 (24.7) 264.6 (58.6)
$^{181}\text{Ta} (n, \gamma)^{182}\text{Ta}$	99.99	20.5	114.5	264.1 (3.6) 1189.0 (16.3) 1221.4 (27.1)

Table 2. Concentrations of Hg, Se and Ta in Moss Lake (ML) and Perch River (PR) atmospheric material fine fractions in ng/m<sup>3</sup> and Charcoal sample (CH) in ng/g.

Element/Sample	ML921217	PR921209	PR921202	CH
	ng/m <sup>3</sup>	ng/m <sup>3</sup>	ng/m <sup>3</sup>	ng/g
Hg	0.014 ± 0.003	0.75 ± 0.02	0.14 ± 0.01	29 ± 5
Se	1.4 ± 0.2	0.43 ± 0.11	1.6 ± 0.3	11000±2000
Ta	< 0.035	< 0.021	< 0.037	280 ± 60

Table 3. Areas under 77.4, 279, 264 and 1221 keV gamma ray peaks for the same samples mentioned in Table 2. The 279\* represents corrected 279.2 keV peak area from Hg-203.

Energy (keV)	Origin of nuclide	ML921217 Counts	PR921209 Counts	PR921202 Counts	CH Counts
77.4	<sup>197</sup> Hg	414±111	27896±195	6201±217	2910±490
279	<sup>203</sup> Hg+ <sup>75</sup> Se	1288±129	6473±233	2690±2167	56900±450
264	<sup>75</sup> Se+ <sup>182</sup> Ta	3120± 160	502±150	3941±173	137400±960
1221	<sup>182</sup> Ta	—	—	—	4600 ± 270
279*	<sup>203</sup> Hg	-22±166	6260±250	1035±201	156±780

# DETERMINING THE WET DEPOSITION OF MERCURY - A COMPARISON OF WEEKLY, BIWEEKLY, AND MONTHLY COLLECTION OF PRECIPITATION SAMPLES

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## ABSTRACT

A bulk sampling equipment for total mercury in precipitation has been used in Sweden since 1989. No significant differences in the mercury concentration in precipitation or the deposition rate are normally found between bulk sampling and wet-only or event samplings. In 1990, a comparison of different collection periods for the bulk sampling equipment revealed no significant difference between weekly, biweekly, and monthly sampling.

## INTRODUCTION

Today, on a regional scale, atmospheric input of mercury constitutes most of the total load on our ecosystems. It is also well recognized that mercury is transported by air masses over long distances.<sup>1</sup> In the Nordic countries, a clearly decreasing south-north gradient in mercury concentration in precipitation exists.<sup>2</sup> In Sweden, a seasonal variability with somewhat elevated mercury concentrations in late winter seems also to be present.<sup>3</sup> In the latter study, bulk collectors were used to sample over monthly periods, from April 1989 to April 1990. The relative variability between triplicate sets of collectors range from 2 to 12 %. A geographical distance of 1 km between two groups of collectors was also included in this variability range. In this paper, we report a comparison of bulk collectors<sup>3,4</sup> operated on alternative weekly, biweekly or monthly basis. Furthermore, a preliminary comparison of the performance of a bulk collector vs. a wet-only collector or manual event samples is performed.

## EXPERIMENTAL TECHNIQUES

The bulk collectors used have previously been described.<sup>3,4</sup> All parts of the collector in contact with the samples were made of borosilicate glass. The area of the bulk collector funnel was 52.8 cm<sup>2</sup>.

The wet-only collector was constructed especially for trace-metal sampling. When used for sampling of mercury in precipitation, all parts of the collector in contact with samples were made of glass. The area of the funnel was 373.1 cm<sup>2</sup>. The manual collection of event samples was performed using a set-up of glass jars with large diameters, which has been described elsewhere.<sup>1</sup> All glass equipment was extensively cleaned according to standard cleaning procedures<sup>1</sup>.

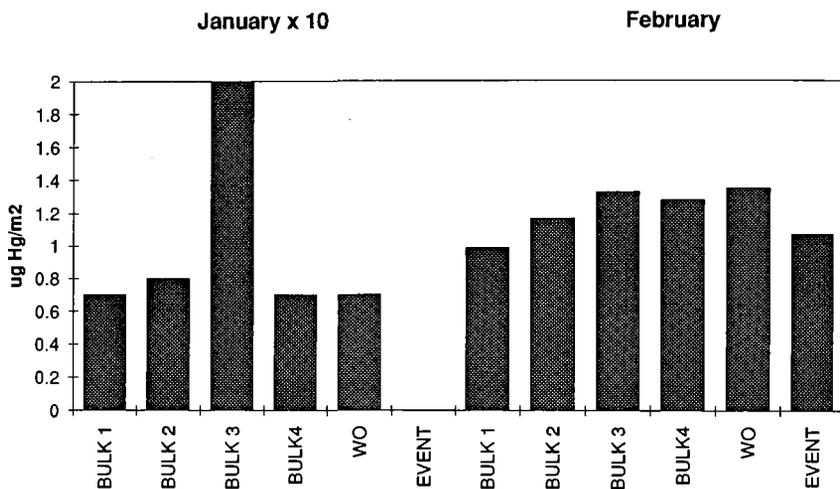
The effect of collection period of the bulk samplers was studied at the Swedish EMEP-station Rörvik, located on the west coast of Sweden near Göteborg, during May to October, 1991. In 1989, the comparison of bulk collectors vs. event sampling was performed at the EMEP-station Aspveten, located on the east coast of Sweden, near Stockholm.

The total mercury concentrations in precipitation collected in 1991 were analyzed after BrCl treatment of the sample followed by SnCl<sub>2</sub> reduction, purging onto gold traps and dual amalgamation Cold Vapor Atomic Fluorescence detection. An Atomic Emission Spectrometry

(AES) detector was used in the analysis of the samples collected in 1989. A representative detection limit for total mercury determination using CVAFS was about  $0.05 \text{ ng L}^{-1}$ , while the precision varied between 5 and 10 %. The detection limit for the AES-method was about  $0.20 \text{ ng L}^{-1}$ .

## RESULTS

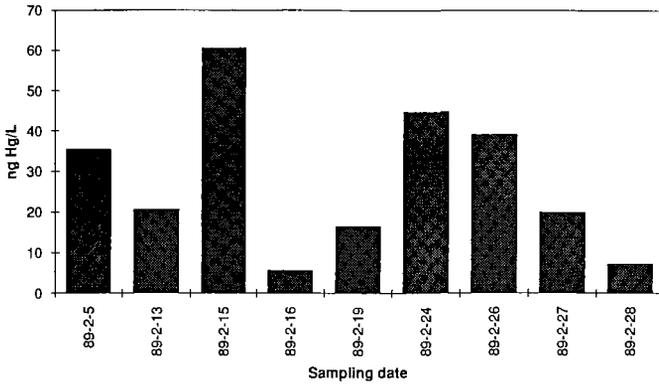
Mean deposition rates derived from the comparison of bulk vs. wet-only collectors is given in Figure 1. No significant difference between the bulk and the wet-only collectors is found.



**Figure 1.** Mercury deposition rates for January and February 1989, derived from a comparison of bulk vs. wet-only collectors or event sampling at Aspvetren.

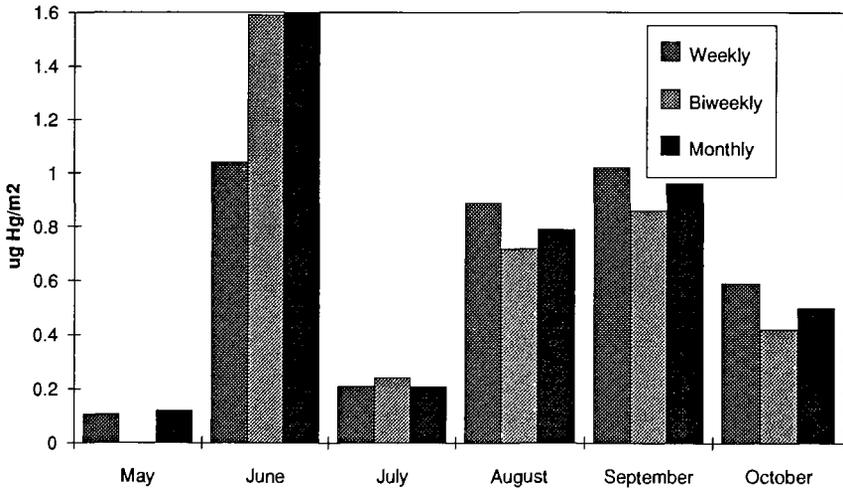
The January value from bulk collector No. 3, is most probably a result of a contamination. These outliers are sometimes observed when using bulk collectors. Therefore, it is highly recommendable to use at least duplicate collectors, in order to be able to find and reject non-representative values.

No detectable differences in mercury deposition rate is present when comparing the results from bulk/wet-only sampling to the event based collection. The event deposition rate for February 1989 is calculated from the measured concentrations at the separate events presented in Figure 2. In this figure, the large variability between mercury levels in various precipitation events, is clearly demonstrated.



**Figure 2. Mercury concentrations in event samples collected at Aspvreten in February 1989.**

A comparison of the mercury data from different collection periods for the bulk sampling of mercury in precipitation revealed no significant differences (Figure 3). No significant dependence between reproducibility and collection time period was found.



**Figure 3. Mercury deposition rates for May to October 1991, at Rörvik, based on weekly, biweekly, and monthly collection periods. The data is derived from a bulk sampling equipment.**

In conclusion, the bulk samplers seems most suitable for monitoring time and/or geographical trends in the atmospheric mercury load to our ecosystems.

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# WET DEPOSITION OF METHYLMERCURY IN SWEDEN

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## ABSTRACT

Monthly samples of precipitation for measurement of methylmercury (MeHg) have been collected since 1990 at several different stations in Sweden. Concentrations of MeHg are generally found to be in the range 0.05 to 0.6 ng L<sup>-1</sup>. A significant gradient exists for MeHg deposition with maximum average rates of 0.29 µg m<sup>-2</sup> yr.<sup>-1</sup> measured in 1992 at stations on the west coast of Sweden and 0.07 µg m<sup>-2</sup> yr.<sup>-1</sup> at the northern sites indicating transport from source areas in Northern and Central Europe.

## INTRODUCTION

Environmental contamination by Hg is mainly linked to the appearance of elevated concentrations of MeHg in freshwater fish. In Sweden, an estimated 10 000 lakes, even in remote areas, are severely affected making the fish caught in them unfit for human consumption.<sup>1,2</sup> Numerous investigations have been conducted in order to determine the causes of these excessive concentrations and the mechanisms regulating the local, regional and global cycling of Hg.<sup>3,4</sup> The only significant source of Hg to remote lake systems with low mineral soil Hg content, is atmospheric deposition which has led to a growing interest in atmospheric concentrations, transformations and deposition patterns of Hg during the last decades.<sup>4,5,6,7</sup> Since the late seventies, a rapid development of techniques for sampling and analysis of mercury in air and precipitation has led to an increased understanding of the atmospheric cycling of this element. However, it is not until recent years that methods have become available for the measurement of MeHg in rain and other natural waters.<sup>8,9,10</sup>

The predominant form of mercury in the atmosphere is elemental mercury (Hg<sup>0</sup>).<sup>3,6</sup> This species is relatively stable with an estimated residence time of around one year. The most probable removal mechanism is aqueous oxidation to water-soluble divalent forms followed by rain-out,<sup>7</sup> although conversion to particulate phase Hg, followed by rain-out, may also occur. The total deposition of Hg is not only related to conversion of gaseous Hg<sup>0</sup> since direct emissions of short-lived gaseous divalent compounds and particulate phase Hg from combustion activities also occurs.<sup>11</sup>

The predominant form of Hg in fish is MeHg. This form is the most toxic Hg species present in the environment. Recent investigations of the cycling of MeHg in a forested catchment in SW Sweden has shown that direct atmospheric deposition to a lake and its catchment may be the dominant source of MeHg in freshwater fish.<sup>12</sup> In the investigated ecosystems, the total soil pools of MeHg are only a fraction of the pools of total inorganic mercury. Despite this, the net transport of MeHg out of the catchment is significant due to an apparent greater mobility of this species in soil,<sup>13</sup> which could constitute a direct route for the uptake of MeHg in fish without the need for a microbial methylation of inorganic mercury. Although the question of the origin of MeHg in fish has not been resolved, continued research on the atmospheric cycling of MeHg including the identification of sources, atmospheric transformations and deposition patterns is essential for our understanding of this environmental problem.

## EXPERIMENTAL TECHNIQUES

Wet deposition samples were collected at 7 sites in Sweden using bulk samplers. The samples were preserved by adding 5 mL HCl to the collection bottle. All glassware in contact with the rainwater were acid-washed and heat treated.

Total mercury concentrations were analyzed after BrCl treatment of the sample followed by SnCl<sub>2</sub> reduction, purging onto gold traps and dual amalgamation Cold Vapor Atomic Fluorescence (CVAFS) as described by Iverfeldt.<sup>5</sup> Methyl mercury was analyzed using a technique similar to that described by Bloom<sup>9</sup> and Fitzgerald and Bloom.<sup>8</sup> This technique is based on the aqueous ethylation of MeHg. Isothermal GC separation followed by pyrolysis and CVAFS detection. The lowest detectable concentration for a 50 mL sample is about 0.05 ng L<sup>-1</sup>.

## RESULTS

A frequency distribution of measured concentrations of MeHg in precipitation collected during the period 1990 to 1992 is given in Figure 1.

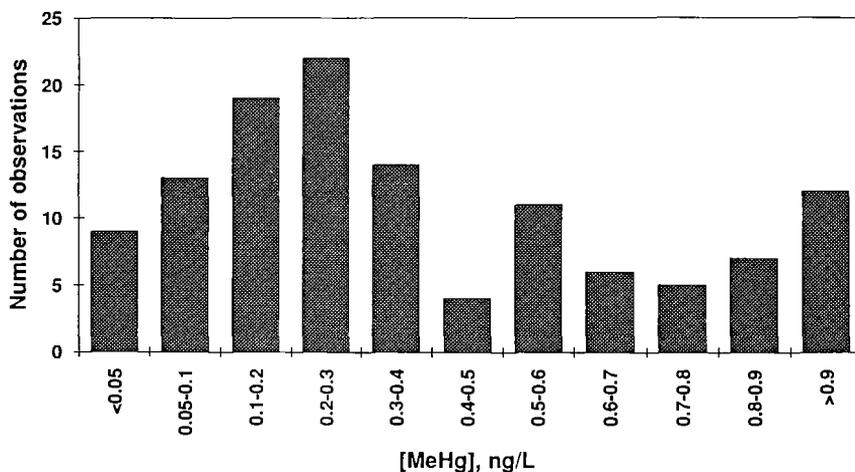


Figure 1. Measured concentrations of methylmercury in precipitation in Sweden. Samples were collected at 7 stations located in the South, East, West and North Sweden.

The concentrations found in precipitation are usually in the range 0.05 to 0.6 ng L<sup>-1</sup>. Occasional values of over 1 ng L<sup>-1</sup> are sometimes found but can in most cases be attributed to contamination from e.g. insects or bird droppings. Due to this reason, only a small number of the concentrations > 0.9 ng L<sup>-1</sup>, reported in Figure 1, were used for the calculations of deposition rates. During the same period, concentrations of total mercury were usually in the range 5 to 30 ng L<sup>-1</sup>, with occasional high

values above 50 ng L<sup>-1</sup>. No direct correlation between the concentrations of MeHg and Hg in rain has been observed. In Table 1, the deposition rates at the four different regions are presented.

**Table I. Annual deposition of methylmercury in different regions of Sweden, 1992.**

Region	Deposition $\mu\text{g m}^{-2} \text{ yr}^{-1}$
South	0.19
West	0.29
East	0.20
North	0.07

A clear gradient can be seen with higher deposition fluxes in the Southern, Eastern and Western regions compared to the Northern region. A similar trend has been noted both for gaseous mercury and deposition of total mercury.<sup>5</sup>

## DISCUSSION

The sources of atmospheric methyl mercury are not known. Attempts to measure gaseous MeHg have only been partly successful, due to the very low concentrations present in air. Recently reported concentrations in ambient air are usually below 0.1 ng m<sup>-3</sup>.<sup>8,14</sup> These concentrations, if true, are sufficiently high to explain the observed concentrations in rainwater, based on thermodynamic considerations.

The deposition gradient of MeHg over Sweden is somewhat sharper than the corresponding gradient for total mercury. This could lead to the suggestion that MeHg is more efficiently washed out from air. Brosset<sup>15</sup> has suggested that measured concentrations of gaseous mercury in air are a function of a uniform background concentration with events of higher concentrations related to anthropogenic activities, such as coal burning in northern and central Europe. Very high gas phase concentrations (1 to 5 ng m<sup>-3</sup>) of MeHg have been reported from air around coal fired power plants, which indicates that this may be a significant source.<sup>16</sup> However, since other sources are possible, such as formation in photochemical processes in air, further studies are needed before the origin of atmospheric MeHg can be resolved

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***Session 14***

***Oxidants in the Atmosphere***

**PEROXYACETYL NITRATE CONCENTRATIONS AT SUBURBAN AND  
DOWNTOWN LOCATIONS IN ATLANTA, GA**

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**ABSTRACT**

Ambient levels of peroxyacetyl nitrate (PAN) were measured simultaneously in Atlanta at a downtown and at a suburban location during August 1992. PAN concentrations were typically lower and daily PAN maxima were observed earlier at the suburban location than at the downtown location. While maximum PAN concentrations for the entire measurement period were similar for both sites, daily PAN concentrations showed more variability at the suburban site than at the downtown site. Diurnal profiles for high ozone (maximum  $O_3 > 80$  ppbv) and low ozone (maximum  $O_3 < 80$  ppbv) days for the two sites showed that PAN concentrations were similar for the two sites during high  $O_3$  episodes. On low ozone days, however, PAN concentrations were significantly lower at the suburban site with maxima similar to those reported for rural Eastern U.S. sites. PAN concentrations at the suburban location for low ozone days were similar to those reported for both a Northeastern U.S. rural site (Scotia, PA) and a Southeastern U.S. rural site (site SONIA). On high  $O_3$  days the concentrations were similar to those of downtown Atlanta. Higher order peroxyacetyl nitrates (PPN and MPAN) were detected at the downtown location with some regularity but were detected very infrequently at the suburban location also suggesting that peroxyacetyl nitrate precursor concentrations were more abundant in the downtown area.

*Introduction*

As part of the Southern Oxidants Study-Southern Oxidants Research Program on Ozone Non-Attainment (SOS-SORP/ONA), an intensive field study was conducted in Atlanta, GA during July and August, 1992. As part of SOS-SORP/ONA, peroxyacetyl nitrate (PAN) was measured at two locations in the metropolitan Atlanta area. PAN is a photochemical oxidant formed by reaction of peroxyacetyl radical with nitrogen dioxide ( $NO_2$ ). PAN is an eye irritant(1), a phytotoxin(2), and an important constituent of  $NO_y$  ( $NO_y = NO + NO_2 + HONO + HNO_3 + N_2O_5 + PAN + NO_3 +$  organic nitrates) in the lower troposphere, a major constituent of  $NO_y$  in the middle troposphere(3), and is the dominant component of  $NO_y$  in the Arctic(4). PAN decomposes rapidly at elevated temperatures ( $> 25^\circ C$ ) and when it does so in a  $NO_2$  deficient atmosphere will release  $NO_2$  and peroxyacetyl radicals. Thus PAN can be an important early morning source of free radicals which quickly initiate photochemistry(5).

In this paper, PAN concentrations at a suburban location and a downtown location within metropolitan Atlanta, GA will be examined. The measurements of PAN at two locations in Atlanta provides a basis for a better understanding of the temporal and spatial distribution of PAN in a large urban area. PAN and  $NO_2$  concentrations, in conjunction with reaction rate constants, will be used to estimate the peroxyacetyl radical concentrations at the suburban site and the results will be compared to those from two rural sites in the Eastern U.S. Simple and multiple linear regression analysis of PAN on total non-methane hydrocarbon (TNMHC), oxides of nitrogen ( $NO_x$ ) and  $O_3$  concentrations at the suburban site will be used to estimate the relative dependence of the two photochemical oxidants, PAN and  $O_3$ , on their precursors. A better understanding of PAN concentrations and the relationship between PAN and its precursors are useful in the development of models used for oxidant control.

### *Experimental Methods*

PAN was measured at two sites in the metropolitan Atlanta area by two different groups of researchers. The suburban location was South Dekalb Community College and the downtown location was the campus of the Georgia Institute of Technology. The two sites are some 20 km apart and are along the prevailing wind direction when the winds are from the Southeast or Northwest. PAN was measured by gas chromatography with electron capture detection (GC-ECD) at both locations. An SRI Model 8610 gas chromatograph and a Valco Model 140 BN electron capture detector were used to measure PAN at the downtown site and a custom-built gas chromatograph using a Valco Model 140 BN electron capture detector were used to measure PAN at the suburban location. The two PAN analyzers are described in detail elsewhere(6,7).

O<sub>3</sub>, NO, NO<sub>x</sub>, carbon monoxide (CO), sulfur dioxide (SO<sub>2</sub>), speciated volatile organic compounds (VOC), and standard meteorological data were also collected at the two locations. The VOC at the suburban location were measured by NCSU but the other trace gas measurements and meteorology were collected by the Georgia Environmental Protection Department and the Georgia Institute of Technology (GIT).

An inter comparison between the two instruments was conducted to validate the comparison of PAN measurements from the two PAN analyzers. The two analyzers were collocated in a trailer on the campus of GIT and were set up to sample ambient air through identical lengths of Teflon sample line. The two instruments had been independently calibrated using different techniques. Chemiluminescent detection of a PAN sample obtained from the diffusion of liquid PAN into purified air was used to calibrate the DGA instrument. Bag dilution of a high concentration gas-phase PAN sample; generated by chlorine atom initiated oxidation of acetaldehyde in the presence of NO<sub>2</sub> and quantified by infrared spectroscopy; was used to calibrate the NCSU instrument. The inter comparison showed that the two instruments tracked each other well and were in close agreement on PAN concentration. A linear regression of the data yielded the following results:  $NCSU_{PAN} = 1.33 DGAPAN - 0.04$  ppbv;  $R^2 = 0.947$  and  $n = 54$ . These results show the two instruments to be within 16.5 % of the mean of the measurements which is within the combined uncertainty (15-20%) of the PAN measurements in the ambient range found in Atlanta.(6)

## **RESULTS AND DISCUSSION**

### *PAN concentrations*

The composite diurnal profile for the suburban and downtown sites are shown in Figure 1. The composite diurnal profile is obtained by averaging the PAN concentration for each specific hour of each day over the entire measurement period. PAN exhibited strong diurnal variation at both the suburban and downtown locations with pre-dawn morning minima often near the limit of detection and with late afternoon maxima typically between 1600 and 1800 EDT. PAN concentrations downtown ranged from below the limit of detection to a maximum of 2.9 ppbv and the average concentration was  $0.43 \pm 0.47$  ppbv (n=817). Average daytime concentration (0900 to 2000 EDT) was  $0.71 \pm 0.53$  ppbv. Daily maxima exceeding 2 ppbv were observed on eight days. PAN concentrations at the suburban location ranged from below the limit of detection to a maximum of 3.10 ppbv with an average concentration of  $0.23 \pm 0.20$  ppbv. Average daytime concentration (0900 to 2000 EDT) was  $0.39 \pm 0.16$  ppbv. Daily PAN maxima exceeded 2 ppbv on two days and exceeded 1 ppbv on 7 days.

### *PAN concentrations on high and low ozone days at the two locations*

The composite diurnal profiles of the suburban and downtown sites were segregated into high ozone (ozone concentration > 80 ppbv) and low ozone (ozone concentration < 80 ppbv) days and the results are shown in Figure 2. Both locations exhibited variation in the shape and magnitude of the PAN diurnal profile under the two different data sets. At both locations the PAN maximum on high ozone days was of greater magnitude as would be expected.

The increase in the maximum for the suburban site, however, was much more dramatic than that for the downtown site. The larger increase in PAN concentrations at the suburban location on high ozone days may be attributed to the greater variability in the abundance of PAN precursors available at the site. Figure 3 shows the wind direction for each of the high ozone days at the suburban site. The prevailing local surface wind direction on the high ozone days was generally from the southwest sector. Atlanta's Hartsfield International Airport and the surrounding area of heavy anthropogenic impact is ~ 2 miles from the suburban site in this direction and likely contributes heavily to PAN precursor concentrations when the wind is out of the southwest. The predominant wind direction at the suburban site on low ozone days was east/southeast putting a predominantly rural low precursor source area upwind of the site. Figure 4 compares the low ozone PAN profile at the suburban site to that of a rural site in North Carolina. The daily maximum PAN concentrations are quite similar suggesting that when the predominant wind is from rural areas PAN profiles at the suburban site are indicative of a regional PAN background.

Prevailing wind direction is less important for the downtown location, however, because its position near the center of the city leaves it exposed to relatively high precursor concentrations from all directions due to the density of precursor sources surrounding the downtown area. Figure 5 shows the average PAN daily maximum for the two prevailing wind sectors, southwest and east/southeast for both the downtown and suburban locations. At the suburban location the average maximum for southeast wind directions was 0.46 ppbv and for southwest wind directions increased 128.2% to 1.05 ppbv. For the downtown site, however, the increase in PAN maxima from the southeast to southwest sectors was from 1.25 to 1.58 ppbv, a more modest 26.4 % increase. Other evidence that precursors are less abundant at the suburban location include the lack of higher order peroxyacyl nitrates at the suburban location. Both PPN and MPAN were detected at the downtown location but neither were detected at the suburban location.(6)

### *Linear regression analysis of the relative importance of TNMHC and NO<sub>x</sub> to PAN and O<sub>3</sub> production at the suburban site*

Linear regression between the daily PAN maximum, the 9 AM total non-methane hydrocarbon (TNMHC), the morning NO<sub>x</sub> maximum, and the daily O<sub>3</sub> maximum was performed to assess the relative importance of VOC and NO<sub>x</sub> concentrations to PAN and O<sub>3</sub> daily maxima at the suburban site. The data necessary to perform this analysis was only available for the suburban location at the time of this writing. Also, the TNMHC data used is preliminary and has not undergone extensive QA/QC yet but is deemed to be representative of the TNMHC at the suburban location. The results of individual and multiple linear regression of PAN and O<sub>3</sub> against TNMHC and NO<sub>x</sub> are presented in Table I. All regressions resulted in R<sup>2</sup> values explaining significant portions of the variability in the PAN and O<sub>3</sub> daily maxima and all were tested for significance and found to be significant at the 99% confidence level.

PAN and O<sub>3</sub> daily maxima were highly correlated to one another as would be expected from their similar photochemical origins. The correlation of the two photochemical oxidants to TNMHC and NO<sub>x</sub> showed interesting differences, however. R<sup>2</sup> values for the regression of PAN against TNMHC and NO<sub>x</sub> indicate that 40% of the variability in PAN daily maxima can be explained by the variability in the morning TNMHC levels at the suburban site. Morning NO<sub>x</sub> concentrations, however, explain 60% of the variability in the PAN maxima. A multiple regression of PAN against NO<sub>x</sub> and TNMHC only increases the explained variability to 61%. It seems then, that the availability of NO<sub>x</sub> at the suburban location is more influential on the day's PAN maxima than the TNMHC concentrations.

O<sub>3</sub>, on the other hand, is more dependent on the morning TNMHC concentrations than NO<sub>x</sub> availability. TNMHC account for 72% of the variability in the daily O<sub>3</sub> maxima while adding NO<sub>x</sub> to the regression only increases the variability explained to 77%. It is also interesting to note that the intercept for O<sub>3</sub> in all of the O<sub>3</sub> regressions is between 25 and 30 ppbv indicating that this is the background level of O<sub>3</sub> in the suburban Atlanta environment.

## CONCLUSIONS

PAN concentrations were generally higher at the downtown location than at the suburban location and were fairly consistent throughout the study. At the suburban location, however, observed PAN maxima on days where the O<sub>3</sub> concentration exceeded 80 ppbv were similar to those of the downtown location. On days where O<sub>3</sub> did not exceed 80 ppbv PAN concentrations were much lower than downtown concentrations and resembled those reported for rural areas in the Eastern U.S. The position of the suburban site near the edge of the metropolitan area subjected it to different upwind precursor source areas depending on the day's prevailing wind direction. These differing precursor availabilities strongly influenced the PAN concentration for that day. When the suburban site was downwind of more rural areas the PAN diurnal profiles resembled those reported for rural sites in the Eastern U.S. When areas of heavier anthropogenic impact were upwind of the suburban site, however, the PAN diurnal profiles and daily maxima were similar to those observed regularly at the downtown location.

Both PAN and O<sub>3</sub> daily maximum concentrations were regressed against the morning NO<sub>x</sub> and 9am total non-methane hydrocarbons (TNMHC) and were found to be strongly correlated to each of these variables and to each other. PAN was more strongly correlated to NO<sub>x</sub> while O<sub>3</sub> was more strongly correlated to TNMHC. Multiple regression of PAN against NO<sub>x</sub> and TNMHC morning maxima explained 61% of the variability of daily PAN maxima while multiple regression of O<sub>3</sub> against NO<sub>x</sub> and TNMHC morning maxima explained 77% of the variability in the daily O<sub>3</sub> maxima.

The similarity of PAN concentrations suggests that the low ozone day PAN concentrations from the suburban Atlanta location and the average PAN concentrations reported from rural Eastern U.S. sites may be indicative of a regional background PAN profile. The high ozone day PAN concentrations at the suburban location and the regularly higher PAN concentrations at the downtown location are thought to be indicative of urban 'spikes' of higher PAN concentrations within the regional PAN background.

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Table 1.

Regression Equation	R <sup>2</sup>	n
PAN(ppbv) = -0.98(TNMHC) + 6.05(NO <sub>x</sub> ) + 19.97 (O <sub>3</sub> ) - 531	0.77**	25
PAN(ppbv) = 0.42(TNMHC) + 10.17(NO <sub>x</sub> ) - 0.48	0.61**	25
PAN(ppbv) = 1.73(TNMHC) + 195	0.40**	25
PAN(ppbv) = 11.88(NO <sub>x</sub> ) + 28.46	0.60**	25
PAN(ppbv) = 0.0199(O <sub>3</sub> ) - 0.47	0.69**	25
O <sub>3</sub> = 0.07(TNMHC) + 0.21(NO <sub>x</sub> ) + 26.54	0.77**	25
O <sub>3</sub> = 0.49(NO <sub>x</sub> ) + 31.40	0.59**	25
O <sub>3</sub> = 0.097(TNMHC) + 30.5	0.72**	25
O <sub>3</sub> = 0.0608(TNMHC) + 20.8(PAN) + 26.46	0.86**	25

\*\* significant at the 99% confidence limit

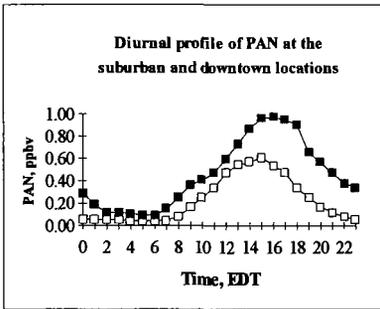


Figure 1. Diurnal profile of PAN at the suburban (open squares) and downtown (dark squares) locations for the entire measurement period.

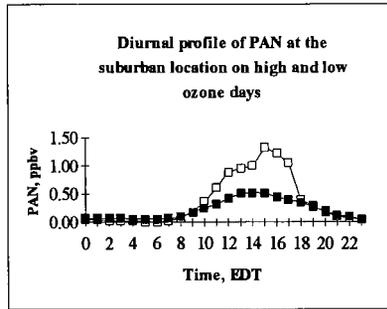


Figure 2a. Diurnal profile of PAN at the suburban location on high ozone (open squares) and low ozone (dark squares) days.

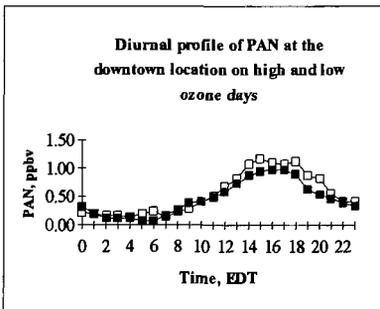


Figure 2b. Diurnal profile of PAN at the downtown location on high ozone (open squares) and low ozone (dark squares) days.

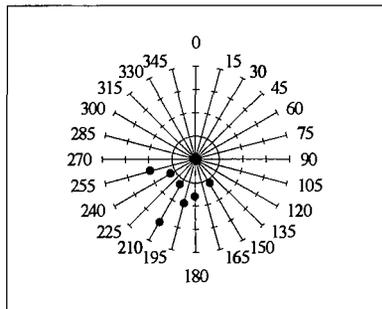


Figure 3. Wind rose showing the day's prevailing wind direction at the suburban site for the 7 days on which the daily PAN maximum at the suburban location exceeded 1.0 ppbv.

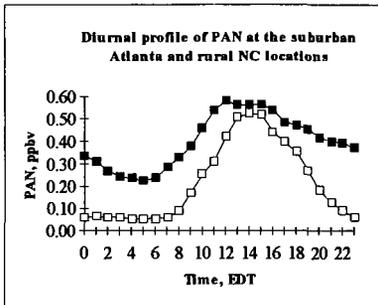


Figure 4. Diurnal profile of PAN at a rural North Carolina site (dark squares) and at the suburban Atlanta site (open squares) on low ozone days.

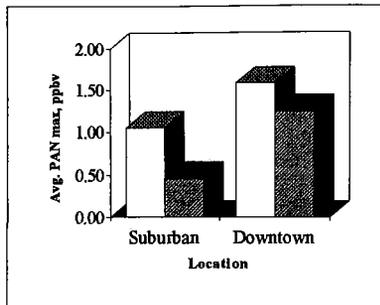


Figure 5. Comparison of average daily PAN maxima for southwesterly winds (open columns) and for southeasterly winds (dark columns) for both the suburban and downtown locations.

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## TRENDS AND ANALYSIS OF AMBIENT NO AND NO<sub>y</sub> CONCENTRATIONS IN RALEIGH, NORTH CAROLINA

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### ABSTRACT

Ambient concentrations of NO and NO<sub>y</sub> as well as O<sub>3</sub> and CO were measured during August 19 to September 1, 1991 in downtown Raleigh, North Carolina as a part of the Southern Oxidants Study-Southern Oxidants Research Program on Ozone Non-Attainment (SOS-SORP/ONA). These measurements were made in an effort to provide insight into the characteristics of nitrogen oxides and their role in the formation of ozone in the urban environment. NO and NO<sub>y</sub> showed bimodal diurnal variations with peaks in the morning (06:00 - 08:00 EST) and in the late evening (21:00 - 23:00 EST). These peaks at this urban site correspond to the coupled effects of rush hour traffic and meteorological conditions (i.e., variation of mixing height and dispersion conditions). The overall average NO and NO<sub>y</sub> concentrations were found to be  $6.1 \pm 5.4$  ppbv (range: 0 to 70 ppbv) and  $14.9 \pm 8.1$  ppbv (range: 0.3 to 110 ppbv), respectively. Average daily maxima of NO and NO<sub>y</sub> (18.3 ppbv and 27.4 ppbv) occurred during the morning. O<sub>3</sub> showed a diurnal variation with a maximum in the afternoon between 14:00 and 16:00 EST: mean concentration  $20 \pm 10$  ppbv (range: 1 to 62 ppbv). Maximum O<sub>3</sub> and CO concentrations during weekdays result from NO and CO emitted from mobile sources during the morning rush hour. Background CO concentration at Raleigh was 470 ppbv. A strong correlation between CO and NO<sub>y</sub> ( $r^2 = 0.34$ ) was observed. The ratio of CO to NO<sub>y</sub> (~ 16) at the Raleigh site suggests that mobile sources are the major contributor to NO and NO<sub>y</sub> concentrations at the site.

### INTRODUCTION

In the lower atmosphere, nitric oxide (NO) is emitted mainly from anthropogenic sources, i.e., stationary and mobile sources<sup>(1,2)</sup>. NO, in turn, is converted to nitrogen dioxide (NO<sub>2</sub>) by reaction with ozone (O<sub>3</sub>) and peroxy radicals (RO<sub>2</sub>). RO<sub>2</sub> radicals are produced mostly by the reaction of hydroxyl radical (OH) with reactive hydrocarbons, and the photolysis of aldehydes which have both natural and anthropogenic origins. NO<sub>2</sub> is then photolyzed in the atmosphere, and the atomic oxygen released combines with molecule oxygen (O<sub>2</sub>) to form O<sub>3</sub>.

It is believed that a significant fraction of the O<sub>3</sub> in the lower troposphere is photochemically produced *in situ*<sup>(3,4)</sup>. For the past 20 years efforts to reduce ozone concentration, especially in urban areas, have focused on control of anthropogenic hydrocarbon emissions. There is, however, no clear evidence that the expected decrease in ozone concentration has been achieved. Over sixty areas in the United States remain classified by the U.S. Environmental Protection Agency (EPA) as ozone non-attainment areas; twenty four of these areas are in the South. It is not clear whether the failure to decrease O<sub>3</sub> concentration is in the basic control strategy, or an inability to reduce total nonmethane hydrocarbon (NMHC) emissions by the necessary amount to reduce O<sub>3</sub> concentration. The interaction between nitrogen oxides, NMHC and their intermediate oxidation products is complex. In general, the relationship between the formation of ozone and its precursors is non-linear. This non-linearity makes the development of an effective ozone control strategy difficult. Recent work suggests that emissions of other precursor, such as those of the nitrogen oxides, should be considered in ozone control strategy<sup>(5,6)</sup>. There is also experimental evidence to suggest that ozone production in the troposphere is limited by the availability of NO<sub>x</sub> (= NO + NO<sub>2</sub>)<sup>(1)</sup>. Completion of a successful budget for tropospheric ozone, therefore, requires additional information on the fate and distribution of nitrogen oxides species (Ridley and Robinson, 1992).

In this section diurnal patterns in the ambient concentrations of NO and total reactive nitrogen species (NO<sub>y</sub> = NO + NO<sub>2</sub> + NO<sub>3</sub> + N<sub>2</sub>O<sub>5</sub> + HNO<sub>3</sub> + PAN + HNO<sub>2</sub> + NO<sub>3</sub><sup>-</sup> + organic nitrates) measured during late summer at Raleigh, North Carolina are presented. Temporal variations in the concentration of these O<sub>3</sub> precursors is directly related to mobile sources associated with the morning and evening rush-hour traffic. Statistical correlations between NO<sub>y</sub> and CO are also discussed for their source relationship in Raleigh. This work is part of the Southern Oxidant Study-Southern Oxidants Research Programs on Ozone Non-Attainment (SOS-SORP/ONA) sponsored by the U.S. EPA. The SORP/ONA focuses on elucidating the processes responsible for the formation of ozone and other photochemical oxidants in urban and industrial centers in the Southern United States<sup>(7)</sup>. Providing NO and NO<sub>y</sub> data measured as input and boundary conditions for photochemical model contributes to develop an effective O<sub>3</sub> control strategy.

### METHODOLOGY

#### *Sampling site*

The sampling site is in an open field (~ 1600 m<sup>2</sup>) on the St. Augustine College campus, which is less than one mile north of the center of downtown Raleigh, North Carolina (35.9 °N, 78.7 °W, 126.8 m MSL). Raleigh is the capital of North Carolina and most of the state government office buildings, legislature, and capital buildings are concentrated in a one square mile area. In addition, a number of municipal buildings and several federal government buildings are present. Several major state highway arteries criss-cross the downtown area leading to substantial traffic flow throughout the day as well as during the peak rush hours. Located within 3 miles of the downtown area are several colleges, one university, the county hospital, as well as a number of county public schools and shopping complexes. Surrounding inner Raleigh is a four-lane highway complex approximately 10 miles in diameter. This outer loop services traffic from several interstate highways and local commuters. There are no industrial, or municipal power emission sources within 10 miles of the downtown area.

#### *Analytical instrumentation*

Ambient NO and NO<sub>y</sub> concentrations as well as meteorological parameters (temperature, wind speed and wind direction) were monitored during the period August 19, 1991 to September 1, 1991. The hourly averaged concentrations of CO and O<sub>3</sub> were measured the same site by North Carolina Department of Environmental Health and Natural Resources (NC DENHER). All species were sampled at ~ 10 m height above the ground and all instruments for NO, NO<sub>y</sub>, O<sub>3</sub> and CO measurement were kept in a temperature controlled mobile laboratory.

NO and NO<sub>y</sub> were measured simultaneously using a modified two channel commercial chemiluminescent NO/NO<sub>x</sub> detector (TECO 14B/E, Thermo Electron) (8,9). The instrument is based on the reaction between NO and reagent O<sub>3</sub> which produces a chemiluminescence that is detected by a photo multiplier tube. The analyzer has an internal heated (~375 °C) molybdenum catalyst which converts most NO<sub>y</sub> species such as NO<sub>2</sub>, HNO<sub>3</sub>, N<sub>2</sub>O<sub>5</sub> and PAN to NO (8,9). N<sub>2</sub>O, N<sub>2</sub>, and NH<sub>3</sub> are not converted to NO to any appreciable degree. For the laboratory operating conditions, the instrument detection limit was 100 parts per trillion volume (pptv) for both NO and NO<sub>y</sub> (8,9). Instrument calibration was accomplished by standard addition of NO in N<sub>2</sub> (Scott Specialty Gases, Inc., Plumsteadville, PA) via a Multigas Calibration System Model 146 (Thermo Environmental Instruments Inc.; Franklin, MA).

## **RESULTS AND DISCUSSION**

### *Diurnal Variations of NO, NO<sub>y</sub> and O<sub>3</sub>*

The mean of NO, NO<sub>y</sub> and O<sub>3</sub> during this period were 6.1 ± 5.4 ppbv (n = 306), 14.9 ± 8.1 ppbv (n = 307) and 20.1 ± 10.4 ppbv (n = 312), respectively. Concentrations of NO and NO<sub>y</sub> ranged from less than 1 ppbv to 70 ppbv for NO and from 1 ppbv to 110 ppbv for NO<sub>y</sub>. O<sub>3</sub> concentrations ranged from 1 ppbv to 62 ppbv. The meteorology parameters were indicative of late summer at this location with relatively hot afternoon temperatures of ~30 °C, relatively low wind speeds averaging about 1.5 m/sec, and prevailing surface winds from southwest.

Composite diurnal profiles of NO, NO<sub>y</sub> and O<sub>3</sub> are shown in Figure 1. O<sub>3</sub> displayed the typical diurnal variation with maximum concentration in the afternoon between 14:00 and 16:00 EST, and minimum concentration early in the morning (~ 06:00 EST). The increase in O<sub>3</sub> during the morning hours coincides with the decrease in NO concentration. This behavior is consistent with the photochemical production of O<sub>3</sub> from locally emitted precursor species. The decrease in O<sub>3</sub> concentration in the evening probably is the result of dry deposition under the subsiding boundary layer and titration with NO. The average daily maximum concentration of O<sub>3</sub> was 36.4 ± 14.7 ppbv.

Peak in the concentrations of NO and NO<sub>y</sub> coincided with the morning and evening rush-hour traffic (Figure 1). The morning peak was relatively brief lasting between 06:00 - 08:00 EST. Average daily maximums of NO and NO<sub>y</sub> during this period were 18.3 ppbv and 27.4 ppbv, respectively. The peaks associated with evening rush hour started around 18:00 EST, reaching a maximum at 21:00 EST. Average daily maximums of NO and NO<sub>y</sub> between 21:00 - 23:00 EST were 11.5 ppbv and 25.8 ppbv, respectively. The ratio of NO to NO<sub>y</sub> during the morning peak periods (~ 0.7) was higher than the ratio for the remainders of the day (ranged from 0.1 to 0.5). NO is emitted primarily by mobile sources during these peak periods and is converted to NO<sub>2</sub> in the air. Therefore, one would expect a higher contribution of NO to NO<sub>y</sub> during these high NO emission periods. Lower mixing depth and reduced dispersive conditions during these morning and night peak periods may also contribute to the increase of NO and NO<sub>y</sub> for a short time period.

Similar diurnal patterns of NO and NO<sub>y</sub> have been observed at urban sites such as West London, Glasgow and Billingham in the U.K. (10), for Atlanta, GA in U.S.A. (data analysis from database of Summer 1990 Atlanta Ozone Precursor Study conducted by U.S.EPA). In our measurements, NO maximum during evening hours may be associated with meteorology and chemistry, as well as direct emission from rush hour traffic. Concentrations of both NO and NO<sub>y</sub> increase gradually after the evening rush hour (~17:00 EST) and into night (~23:00 EST). The abundance of NO emitted from rush hour traffic may directly increase NO concentration in ambient air. However, no NO peak was found at the evening rush hour. This is attributed to immediate loss of NO by reaction with O<sub>3</sub> which is abundant during the evening rush hour. The decrease of O<sub>3</sub> after rush hour is thought to be evidence of this fact (Figure 1). The steady increase of NO until 23:00 EST may indicate the presence of NO sources (probably continued automobile exhaust during the evening) at the site during the period.

To examine the contribution of NO emitted from the rush hour mobile traffic to the NO peak concentration, diurnal variation of NO, NO<sub>y</sub> and O<sub>3</sub> on weekdays and weekends are presented in Figure 2. On weekends, there were no significant variations of NO and NO<sub>y</sub> concentrations. Only a relatively small variation of O<sub>3</sub> between day and night were found. Both NO and NO<sub>y</sub> mean concentrations were significantly reduced on weekends (0.3 ppbv for NO and 4.8 ppbv for NO<sub>y</sub>) from the daily means for the entire measurement period (6 ppbv for NO and 15 ppbv NO<sub>y</sub>). On the other hand, significant diurnal variations of NO, NO<sub>y</sub> and O<sub>3</sub> were observed on weekdays. NO and NO<sub>y</sub> concentrations during daytime (10:00 to 18:00 EST) were low with average concentrations of NO and NO<sub>y</sub> less than 0.5 ppbv for NO and about 5 ppbv for NO<sub>y</sub>. Average NO and NO<sub>y</sub> for the rest of hours were about 10 ppbv for NO and 20 ppbv of NO<sub>y</sub>. Peak NO concentration on weekdays was two orders of magnitude higher than peak NO concentration on weekends. Low levels of NO and NO<sub>y</sub> during the day is probably due to photochemistry as well as enhanced dispersive conditions. NO reacts with peroxy radicals which are formed mostly from the oxidation of CO and hydrocarbons by OH attack and is converted to NO<sub>2</sub>. Mixing height also is increased and well-mixed conditions exist during daytime. On the other hand, during night time, there is no photochemistry and more stable atmospheric conditions exist. A decrease of NO concentration is observed from 02:00 to 05:00 EST. This decrease is mainly due to the reaction of NO with ozone.

During morning rush hours, the NO<sub>y</sub> peak occurs about 1 hour later than that for NO; however, NO and NO<sub>y</sub> maximum are coincident during nighttime. Examination of NO and NO<sub>2</sub> daily peaks at urban cities in the U.K. (10) showed a similar relationship between daily NO and NO<sub>y</sub> peaks. The coincidence of NO and NO<sub>y</sub> maxima during nighttime reflects the dominant effects of primary emissions of NO and the production of NO<sub>2</sub> by ozone titration of NO together with, possibly, catalytic ambient oxidation at low temperature. These reactions are fast, and will not therefore cause a significant delay between nighttime NO and NO<sub>y</sub> peaks. During the morning rush hour, however, photochemical oxidation processes involving OH attack on hydrocarbons to form peroxy radicals are of increased importance. A contribution from the formation of peroxy radicals could be a reason for the delay between NO and NO<sub>y</sub> peaks, as found previously for the Central London Site (11).

Daily averaged maximum of O<sub>3</sub> concentration on weekdays was found to be ~10 ppbv higher than that on weekends. High NO concentration on weekday mornings may result in greater NO<sub>2</sub> concentration by reaction with peroxy radicals at the site. The level of CO and hydrocarbons in such an urban area may provide enough hydroxyl radical concentration to oxidize NO. Approximately 1 ppmv of CO concentration was observed during weekdays morning hours. Thus, this increase of the maximum O<sub>3</sub> on weekdays is thought to be due to the high NO emission locally emitted during weekday mornings.

#### *CO trends and their relation to NO<sub>y</sub> and O<sub>3</sub> concentrations*

Hourly averaged CO concentrations have little variations in the Raleigh measurements. The hourly averaged CO concentrations during the measurement period vary from 0.2 ppmv to 2.6 ppmv, and the mean and standard deviation was  $0.7 \pm 0.1$  ppmv. CO data measured at the site show the average CO level is higher in the morning and through the night than during day time. Minimum CO concentration occurs around 16:00 EST when photochemical activity is the strongest during the day. The minimum value was considered as CO background concentration at the site.

Examination of hourly averaged CO concentrations during the measurement period show apparently different emission level of CO during morning rush hours. CO concentrations above than 1.2 ppmv were observed during morning rush hours of the 22<sup>nd</sup>, 23<sup>rd</sup> and 29<sup>th</sup> August, 1991 while CO concentrations below than 0.6 ppmv were measured on the rest of the measurement days. CO should effect on O<sub>3</sub> chemistry through oxidation involving radicals and nitrogen oxides in ambient air (12). Atmospheric chemistry behavior including O<sub>3</sub> and NO<sub>x</sub> may differ depending on CO concentration, i.e., under high CO conditions and under low CO conditions. High CO conditions are defined for this study as days where the morning peak time CO concentration is above than 1.2 ppmv. Low CO conditions are defined as days where the morning peak time CO concentration is below than 0.6 ppmv. The mean of CO concentration during the high CO conditions ( $1.2 \pm 0.4$  ppmv) is about twice that during low CO conditions ( $0.5 \pm 0.1$  ppmv). Mean NO and NO<sub>y</sub> concentrations in high CO conditions ( $15.7 \pm 14.2$  ppbv for NO and  $31 \pm 20$  ppbv for NO<sub>y</sub>) are significantly higher than those in low CO conditions ( $1.2 \pm 1.8$  ppbv for NO and  $6.7 \pm 2.9$  ppbv for NO<sub>y</sub>).

High NO concentrations coincident with high CO concentrations are expected because both CO and NO have similar anthropogenic sources (mainly mobile sources) in urban areas. To examine source relationship between CO and NO, correlation between CO and reactive NO<sub>y</sub> concentration measured at Raleigh was shown in Figure 3. A linear regression of hourly average CO and NO<sub>y</sub> concentrations was performed and showed a strong correlation during the measurement period ( $[CO] = 16.3[NO_y] + 470$ ;  $r^2 = 0.53$ ). The regression curve reveals a background CO concentration of 470 ppbv in the Raleigh urban area. It is not surprising that the background of CO at the Raleigh urban site is much higher than the value of 200 ppbv in clean air region of the northern hemisphere (13), because the measurements were made near the downtown of the city where significant anthropogenic sources for CO are expected. The ratio of CO concentration to NO<sub>y</sub> concentration at Raleigh urban site (which is the slope of the regression curve in Figure 3) was 16.3. Average emissions of CO, NO<sub>x</sub> and SO<sub>2</sub> in eastern United States using NAFAP Emission Inventory for summer were summarized, and the average emission ratio of CO and NO<sub>y</sub> in eastern United States during summer was reported as 4.3 (14). A high

emission ratio between CO and NO<sub>y</sub> (CO/NO<sub>y</sub> > 8) indicates mobile sources are dominant while low emission ratios (CO/NO<sub>y</sub> < 1) indicate that point sources are dominant. The ratio of 16.3 observed at Raleigh urban site is close to the emission ratio of CO to NO<sub>y</sub> (16.5) from only the mobile source dominant Denver metropolitan area. Thus, the high ratio of CO to NO<sub>y</sub> at Raleigh urban site suggests that the urban plume in Raleigh is impacted mainly by mobile sources.

Figure 4 shows the diurnal variation of each species for both high and low CO conditions. Maximum ozone in high CO conditions is about 20 ppbv higher than during the low CO conditions even though levels of NO and NO<sub>y</sub> in both cases are similar during daytime hours with NO concentrations of about 1 ppbv and NO<sub>y</sub> concentrations of about 5 ppbv. The increase of maximum ozone concentration in high CO conditions is influenced by the following photochemical factors: (1) significantly higher ambient NO concentration during morning peak time in high CO conditions since NO and CO share sources and the NO is oxidized to form NO<sub>2</sub>; and (2) high CO levels, since ozone can be produced by oxidation of CO in sufficient NO concentration. High CO conditions, therefore, are conducive to greater O<sub>3</sub> formation leading to greater O<sub>3</sub> maxima. On the other hand, minimum ozone levels are lower in high CO conditions than in low CO conditions because ozone is destroyed rapidly by reaction with the higher NO concentrations.

The response of daily maximum O<sub>3</sub> concentration to maximum NO<sub>y</sub> concentration, and the ratio of CO concentration to NO<sub>y</sub> concentration ( $[CO]/[NO_y]$ ) at morning peak hours are shown in Figure 5. Daily maximum O<sub>3</sub> concentrations in the Raleigh urban areas were found to be a function of daily maximum NO<sub>y</sub> concentration and the ratio of CO concentration to NO<sub>y</sub> concentration during the measurement period. Positive correlations between maximum O<sub>3</sub> concentration and maximum NO<sub>y</sub> concentration ( $r^2 = 0.34$ ) and between maximum O<sub>3</sub> concentration and  $[CO]/[NO_y]$  ( $r^2 = 0.47$ ) were observed. These observational-based results suggest that local production of NO from mobile sources at this location contributes to the photochemical production of O<sub>3</sub>.

## SUMMARY AND CONCLUSIONS

The mean NO and NO<sub>y</sub> concentrations were found to be  $6.1 \pm 5.4$  ppb (ranged from 0 to 70 ppbv) and  $14.9 \pm 8.1$  ppbv (ranged from 0.3 to 111 ppbv), respectively. Diurnal patterns of NO and NO<sub>y</sub> observed at Raleigh site is similar to those were observed at urban cities in the U.K.<sup>(10)</sup> and Atlanta, GA in the U.S. (Atlanta Ozone Precursor Study, U.S. EPA, 1990). The peak of NO and NO<sub>y</sub> in the morning was coincident to morning rush hours at the site. The average contribution of NO to NO<sub>y</sub> concentration (NO/NO<sub>y</sub>) was ~ 20 % during the entire measurement period. The high contribution of NO to NO<sub>y</sub> concentration (~ 70 %) during morning rush hours was attributed to mobile sources in the urban area.

Different diurnal patterns of NO and NO<sub>y</sub> between weekdays and weekends was found and mainly due to emission from mobile sources. On weekends no morning peak was observed and both NO (0.3 ppbv) and NO<sub>y</sub> concentrations (4.8 ppbv) were significantly reduced from daily mean concentrations for the entire measurement period (6 ppbv for NO and 15 ppbv for NO<sub>y</sub>). Daily averaged maximum of O<sub>3</sub> concentration during weekdays was found to be 10 ppbv higher than that during the weekends. Slightly variations of hourly averaged CO concentrations was observed during entire measurement period (0.2 - 2.6 ppmv; mean and standard deviation =  $0.7 \pm 0.1$  ppmv). However, relatively high CO concentrations above than 1.2 ppmv during the morning rush hours were observed. Increase of maximum O<sub>3</sub> in weekdays and high CO conditions may result from increase of photochemical formation of O<sub>3</sub> due to high NO and CO level during morning rush hours at the site.

Strong correlation between CO and NO<sub>y</sub> concentrations ( $r^2 = 0.53$ ) was found during measurement period. The background CO concentration was 470 ppbv. The observed ratio of CO to NO<sub>y</sub> concentration at Raleigh urban site, 16.3, was close to the emission ratio of CO to NO<sub>y</sub> (16.5) which was observed from the mobile source dominant Denver metropolitan area<sup>(14)</sup>. This ratio suggests that the air mass at Raleigh site is characterized by mainly mobile sources. Daily maximums of O<sub>3</sub> were correlated to daily maximums of NO<sub>y</sub> ( $r^2 = 0.34$ ), and the  $[CO]/[NO_y]$  ( $r^2 = 0.47$ ) during the measurement period. These observational-based results suggest that local production of NO from mobile sources at this location contributes to the photochemical production of O<sub>3</sub>.

The results from Raleigh urban site demonstrate that the emission of NO from mobile sources during morning rush hours may be an important source of atmospheric NO concentration, and that this locally produced NO concentration may increase the maximum O<sub>3</sub> during the day. Without hydrocarbon data analysis, however, there are uncertainties in the discussion of photochemical production of O<sub>3</sub>. Thus it is clear that more comprehensive data analysis of nitrogen species as well as hydrocarbons emitted in urban areas are needed to enhance our understanding of O<sub>3</sub> photochemistry in the urban environment. It is that the analysis and discussions of the nitrogen oxides measurements made at Raleigh site will contribute to the development of improved methodologies for characterizing the causes of ozone non-attainment in a given urban area.

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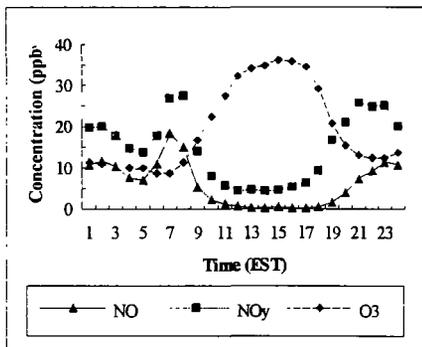


Figure 1. Composite diurnal profiles of NO, NO<sub>y</sub> and O<sub>3</sub> at Raleigh, N.C.

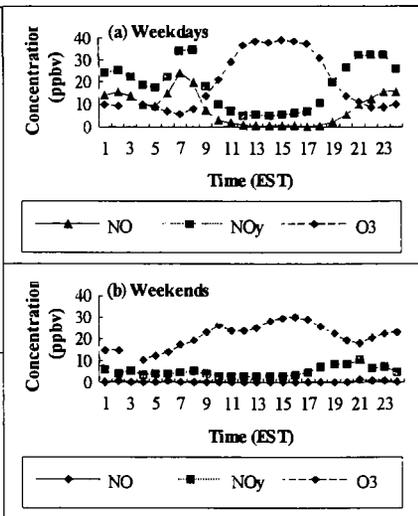


Figure 2. Composite diurnal profiles of NO, NO<sub>y</sub> and O<sub>3</sub> for (a) weekdays and (b) weekends at Raleigh, N.C.

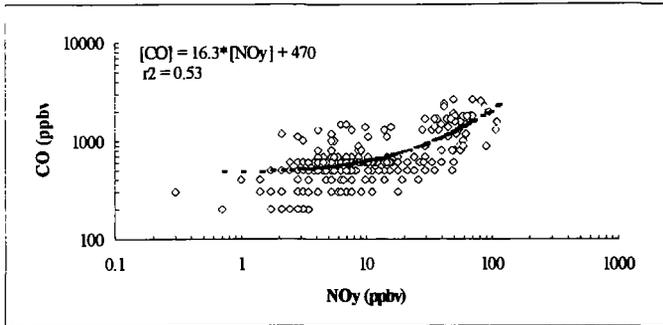


Figure 3. Correlation between [CO] and [NOy] on a log-log plot at Raleigh, North Carolina. Individual data points are from hourly averages during 8/19/91-9/1/91.

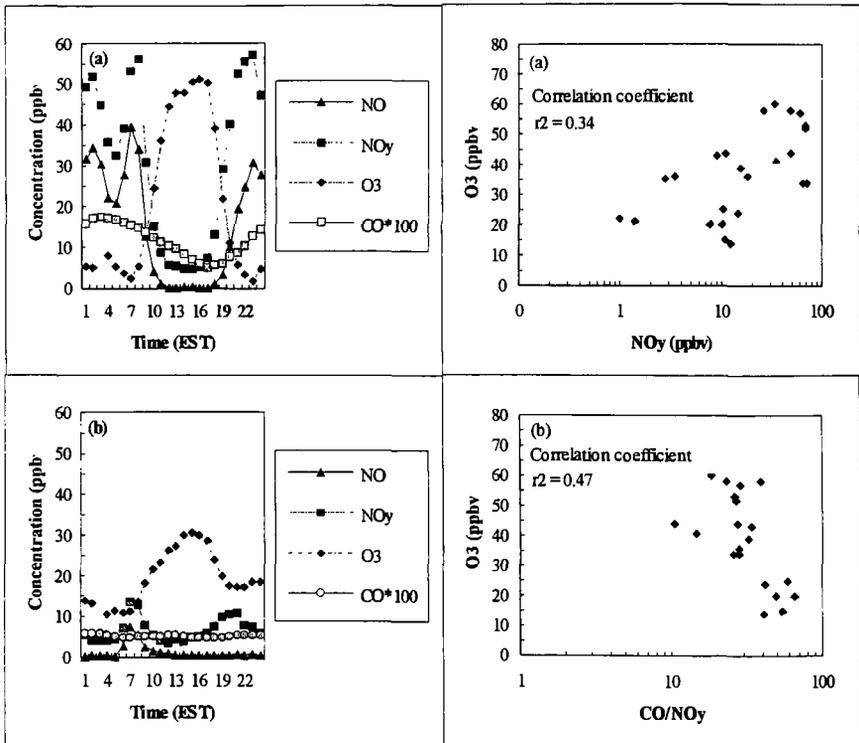


Figure 4. Composite diurnal variations of NO, NOy, O3 and CO for (a) high CO and (b) low CO conditions at Raleigh, N.C.

Figure 5. Correlations between daily maximum of [O3] and (a) [NOy]; (b) the ratio of [CO] to [NOy] at rush hour in the morning on a semi-log plot.

## Gaseous Hydrogen Peroxide Concentrations in the Central Piedmont Region of North Carolina

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### ABSTRACT

Gas-phase total peroxides and hydrogen peroxide were monitored in the ambient air at Candor, N.C. during the summer of 1991 and 1992. Gas phase  $\text{H}_2\text{O}_2$  concentration measured from below the level of detection ( $\sim 0.1$  ppbv) to about 2.2 ppbv. Concentrations of hydrogen peroxide showed a diurnal variation with maximum concentrations in the afternoon ( $\sim 1.5$  ppbv) and was found to be affected by the concentrations of other trace gases as well as meteorological parameters. Decrease of gas phase concentrations was observed during wet atmospheric conditions. Evaluation of the data with respect to meteorological conditions and the concentrations of other pollutants showed that  $\text{H}_2\text{O}_2$  concentrations were associated with long-range transport of polluted air masses from the surrounding areas. Evidence of night time  $\text{H}_2\text{O}_2$  resulting from breakdown in the stability of the nocturnal boundary layer was found. Linear regression analysis of hourly average, daytime average and daily maximum  $\text{O}_3$  on  $\text{H}_2\text{O}_2$  indicates that at this rural site the formation of  $\text{H}_2\text{O}_2$  is favored by increasing ozone and an ozone concentration of  $\sim 18$  ppbv for 1 ppbv of  $\text{H}_2\text{O}_2$  was obtained.

### INTRODUCTION

Gas-phase total peroxides and hydrogen peroxide were monitored in the ambient air at Candor, N.C. as part of Southern Oxidant Study (SOS) project SONIA funded by the U.S. Environmental Protection Agency during mid July to mid August in 1991 and the month of June to early July in 1992. The measurements were made using continuous dual-channel fluorometric analyzer based on the horse radish peroxidase method (1). Hydrogen peroxide is a secondary photochemical oxidant formed by  $\text{HO}_2$  radical recombination. Its production is highly sensitive to the competing reaction of  $\text{NO}$  and  $\text{HO}_2$  and thus its production rate is a complex function of the level of photochemical activity and air mass age (2). Modelling studies have shown that the generation of  $\text{H}_2\text{O}_2$  is affected by the presence of atmospheric pollutants such as  $\text{NO}_x$ , VOC, and  $\text{CO}$ , and by meteorological parameters such as solar radiation, temperature, and water vapor content (2-4). It is also highly soluble in water (Henry's Law constant  $H = \sim 10^5 \text{ M/atm}$ ) and thus is easily removed from the atmosphere by wet deposition, including rain scavenging, fog and mist droplet scavenging (5).

In this paper, the role of meteorology on the diurnal variation of  $\text{H}_2\text{O}_2$  is examined. The relationship between  $\text{H}_2\text{O}_2$ , and chemical and physical processes is examined on the basis of observational based statistical analysis. Finally, the  $\text{H}_2\text{O}_2$  concentrations are compared to ozone levels at this rural site .

## RESULTS AND DISCUSSION

A statistical summary of  $\text{H}_2\text{O}_2$  concentrations for both years is given in table 1.  $\text{H}_2\text{O}_2$  exhibits a distinct diurnal trend with significantly higher day time  $\text{H}_2\text{O}_2$  levels than the night time levels. The daytime mean as well maximum  $\text{H}_2\text{O}_2$  levels are higher in 1991 than 1992. But the median is same for both years indicating that during the 1991 measurement period few episodic levels were observed. Fig 1. shows the composite diurnal profile of both  $\text{H}_2\text{O}_2$  as well as ozone for the entire measurement period during '91 and '92. The smooth rise during the morning to the afternoon is in accordance with expected photochemical production. Peak concentrations in both ozone as well  $\text{H}_2\text{O}_2$  were reached during the late afternoon hours (1400-1600 EST) and the minimum was observed about 0500-0800 EST.

Though the maxima and minima are collocated in time, there is a considerable amount of background ozone surviving the night whereas  $\text{H}_2\text{O}_2$  levels drop to the detection limits. Also the fall in the  $\text{H}_2\text{O}_2$  concentrations is more rapid and takes place earlier when compared to ozone. Low night time  $\text{H}_2\text{O}_2$  levels have been observed in the past by many researchers and cannot be accounted for by just surface losses due to dry deposition. One explanation put forward by Hastie et al., (6) is that during the night time, aqueous aerosols, formed as a result of water condensing on atmospheric particles at the onset of nocturnal inversion, efficiently scavenge the highly soluble  $\text{H}_2\text{O}_2$ . We found a strong anticorrelation between  $\text{H}_2\text{O}_2$  concentrations and the relative humidity ( $r = -0.83$  and  $-0.77$  during '91 and '92 respectively) and the composite diurnal profile is given figure 2. From an examination of figure 2, it is clear that  $\text{H}_2\text{O}_2$  begins to rise only after the relative humidity has fallen significantly low  $\sim 70$ -65% and the rapid fall is coincident with increasing relative humidity. This apparent higher sensitivity of  $\text{H}_2\text{O}_2$  to relative humidity is explained by its higher solubility. This points to the fact that after sunset, due to the radiative cooling of the earth's surface, the increased relative humidity effectively scavenges the gas phase  $\text{H}_2\text{O}_2$  trapped in the shallow nocturnal boundary layer. Thus the concentration of gaseous  $\text{H}_2\text{O}_2$  trapped within the inversion is lost by dry as well as deposition and the concentration  $\text{H}_2\text{O}_2$  measured falls without replenishment from above.

Occasionally, however, a secondary night time peak in  $\text{H}_2\text{O}_2$  accompanied by a secondary peak in ozone was observed (figure 3). From an examination of the  $\text{H}_2\text{O}_2$  profile together with meteorology, the peak was found to be the result of a weak nocturnal boundary layer. Downward mixing of undepleted air from aloft under such conditions can result in high night time concentrations. Evidence of decrease in gas phase  $\text{H}_2\text{O}_2$  concentrations during rain, fog or cloud formation was also found. This has been attributed to the reduction in solar flux by clouds and also to cloud scavenging of  $\text{H}_2\text{O}_2$  due to its high solubility (7) .

Linear relationship between  $\text{H}_2\text{O}_2$  and other measured physico-chemical variables were examined. It was found that among all the environmental parameters,  $\text{H}_2\text{O}_2$  was

most strongly negatively correlated to relative humidity as already explained above. It was also found to have a strong correlation to solar radiation and temperature ( $r=0.61$  and  $0.87$  and  $r=0.68$  and  $0.67$  respectively for '91 and '92). This is consistent with modelling studies (2,4). High solar radiation levels result in intense photochemical reactions of chemical species resulting in the formation of free radicals including  $\text{HO}_2$ .  $\text{H}_2\text{O}_2$  was found to be strongly correlated to ozone ( $r=0.78$  and  $0.63$  respectively for '91 and '92). This is not surprising as both are photochemical products in air. Also, in a clean atmosphere, the photolysis of ozone is the major source of radicals (2), and thus is the source of  $\text{HO}_2$  radicals. During 1992 no significant correlation between  $\text{H}_2\text{O}_2$  and other primary pollutant species like  $\text{NO}_x$ , CO and  $\text{SO}_2$  were found. This is expected because the primary pollutant concentrations are low at this rural site. However, during the 1991 measurement period significant negative correlation between  $\text{NO}_x$  and  $\text{H}_2\text{O}_2$  was found and a surprising positive correlation between  $\text{H}_2\text{O}_2$  and  $\text{SO}_2$  was observed ( $r=0.45$ ). A positive correlation between ozone and  $\text{SO}_2$  was also found ( $r=0.56$ ) (Fig 4.). This suggests the role of long range transport of pollutants to this rural site. An examination of 48 hour back trajectories of the air masses arriving at the site showed significantly higher peroxide concentration when the air mass was continental in origin than when the air mass originated over the oceans.

Hourly averaged, daytime hourly averaged and daily maximum  $\text{O}_3$  was regressed on  $\text{H}_2\text{O}_2$ . The results are given in table 2. The slopes obtained from the regression equation are comparable for both the years indicating that similar conditions favoring the formation of both ozone and  $\text{H}_2\text{O}_2$  prevailed during the two years. For the daytime averaged data  $\sim 18$  ppbv of ozone for 1 ppbv of  $\text{H}_2\text{O}_2$  was obtained. Also when the daily maximum was considered, the  $R^2$  obtained is considerably higher. This indicates that the formation of  $\text{H}_2\text{O}_2$  is favored by increasing ozone concentrations in this rural area and the conditions favoring the formation of ozone also favor the formation of  $\text{H}_2\text{O}_2$ .

## CONCLUSIONS

$\text{H}_2\text{O}_2$  concentrations exhibited a diurnal profile with maxima during the late afternoon indicative of photochemical formation in the atmosphere. The minima which was close to the detection limit of the instrument was observed about 0500-0800 EST coincident with high relative humidity. It was reasoned that during the night time, in the presence of a nocturnal inversion, aqueous droplets efficiently scavenged gaseous  $\text{H}_2\text{O}_2$  and the concentration dropped due to wet deposition and lack of replenishment from the mixed layer. However, during conditions of a weak nocturnal boundary layer, downward mixing of undepleted air from aloft tended to restore the concentration.

$\text{H}_2\text{O}_2$  was found to be highly correlated to solar radiation, temperature and ozone among the various environmental parameters measured. During the 1991 measurement period, a high correlation between  $\text{H}_2\text{O}_2$  and  $\text{SO}_2$  as well as ozone and  $\text{SO}_2$  was found indicating the role of long range transport of pollutants to this rural site.

Ozone was regressed on hourly averaged, daytime average and daily maximum  $\text{H}_2\text{O}_2$ . When daytime hourly average ozone was regressed on  $\text{H}_2\text{O}_2$ , it was found that for the daytime average data  $\sim 18$  ppbv of ozone was obtained for a ppbv of  $\text{H}_2\text{O}_2$ . Regression of daily maximum ozone on  $\text{H}_2\text{O}_2$  gave a high  $R^2$  indicating that at this rural site the formation of  $\text{H}_2\text{O}_2$  is favored by increasing ozone.

## ACKNOWLEDGEMENTS

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*Table 1. Statistical summary of measurements made at Candor during '91 and '92*

Period	N	Mean	SD	Median	Max	Min
1991	296	0.41	0.51	0.21	2.19	<LOD*
Days	156	0.64	0.56	0.42	2.19	<LOD
Nights	140	0.16	0.18	0.10	0.94	<LOD
1992	303	0.35	0.36	0.23	1.60	<LOD
Days	164	0.52	0.36	0.43	1.60	<LOD
Nights	139	0.15	0.22	0.10	1.05	<LOD

\* LOD=Level of detection

Table 2. Regression analysis of hourly average, daytime and daily max H<sub>2</sub>O<sub>2</sub> and ozone.

	Hourly Average	Daytime	Daily Maximum
CANDOR 1991			
Regression Eqtn	O <sub>3</sub> =25.26+26.78H <sub>2</sub> O <sub>2</sub>	O <sub>3</sub> =32.79+19.14H <sub>2</sub> O <sub>2</sub>	O <sub>3</sub> =29.17+20.57H <sub>2</sub> O <sub>2</sub>
R <sup>2</sup>	0.60	0.57	0.69
n	293	107	13
CANDOR 1992			
Regression Eqtn	O <sub>3</sub> =34.06+29.19H <sub>2</sub> O <sub>2</sub>	O <sub>3</sub> =43.69+18.23H <sub>2</sub> O <sub>2</sub>	O <sub>3</sub> =42.14+21.42H <sub>2</sub> O <sub>2</sub>
R <sup>2</sup>	0.39	0.35	0.48
n	301	120	8

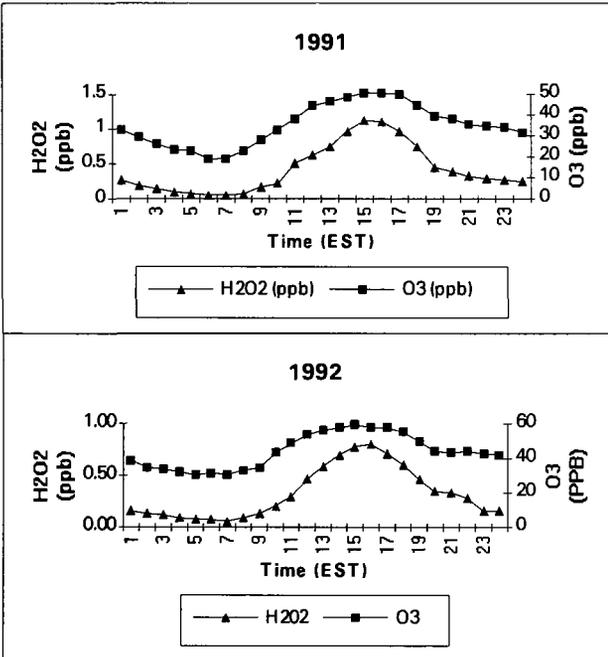


Figure 1. Composite diurnal variations of H<sub>2</sub>O<sub>2</sub> and ozone.

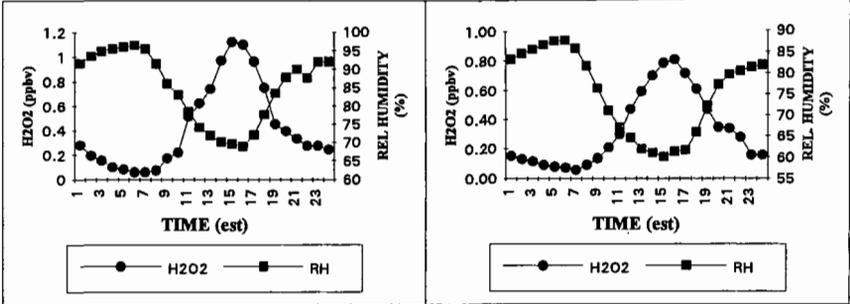


Fig 2. Figure showing the inverse relationship between H2O2 and Relative Humidity

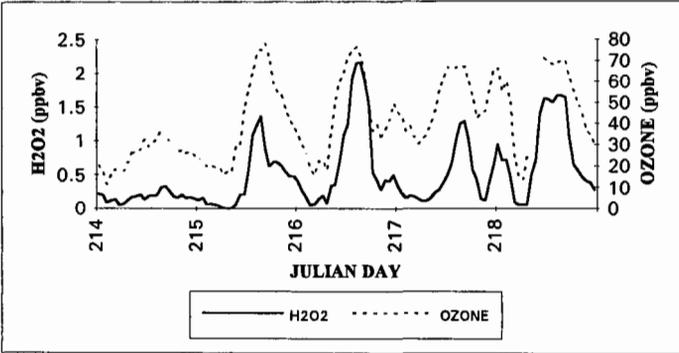


Fig 3. Figure showing the secondary night time peak in H2O2 and ozone

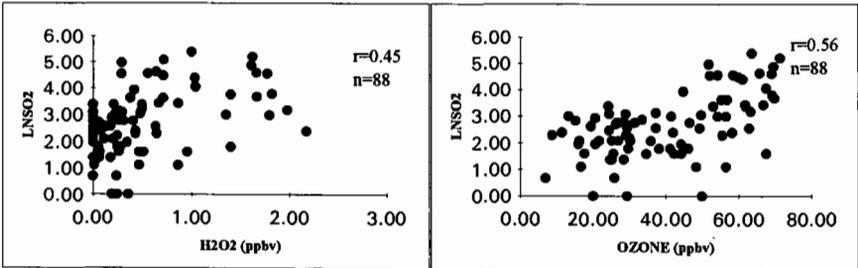


Fig 4. Positive correlations between H2O2 and SO2 and ozone and H2O2

*Session 15*

*FTIR and Remote Sensing*

## FIELD TESTING OF TWO VOC EMISSION RATE ESTIMATION METHODS

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### ABSTRACT

Two methods of estimating the VOC emission rate are described. The methods are being field tested at a flat, grass-covered site by the University of Kansas, in cooperation with Region VII of the U.S.EPA and Kansas State University. Initial testing is conducted using a single point source; later phases of the study will focus on simulated and actual area sources, in an attempt to extend applicability to Superfund sites. Both methods use path-integrated VOC concentrations and a form of the integrated Gaussian dispersion equation to produce an estimated rate. Both methods attempt to overcome problems associated with the direct application of the Gaussian equation through their use of meteorological data: Model 1 uses means of wind speed and wind direction for the duration of the test period; Model 2 uses one-minute means of those variables. Based on data from all tests, Model 1 provides an increase in emission rate estimation accuracy over the direct application of the integrated Gaussian equation; Model 2 provides a slight additional increase. Based on data from only those tests during which the assumptions used to derive the integrated Gaussian expression were violated, Model 1 provides a significant increase in estimation accuracy; Model 2 provides a significant additional increase. Therefore, the models described in this paper allow the integrated Gaussian equation to be applied more accurately in cases where its underlying assumptions are violated. Estimation accuracy is better under class B stability conditions than under more stable conditions; Model 2 provides increased accuracy over Model 1 as conditions become more unstable. Model performance is better at 100 and 150 meters downwind distance than at 50 meters. Model 1 provides a significant improvement over the direct application of the integrated Gaussian equation at 150 meters; Model 2 provides a significant additional improvement.

### INTRODUCTION

The University of Kansas (KU) has assisted Region VII of the U.S.EPA in the development of a volatile organic compound (VOC) monitoring capability during the last several years<sup>1</sup>. As a part of that work, KU and Region VII have field tested and refined a method consisting of whole-air sampling in evacuated stainless steel canisters and gas chromatographic (GC) analysis. In addition, KU has assisted in the field testing of an open-path Fourier Transform Infrared spectroscopic (FTIR) method developed by Kansas State University (KSU) and Region VII<sup>2</sup>. Results have shown both methods to be viable for ambient air VOC monitoring.

KU, in cooperation with KSU and Region VII, has undertaken to extend the capabilities of the two methods by using them to estimate VOC emission rates from various types of sources, with emphasis on the applicability to Superfund sites. To accomplish this goal, KU is conducting field tests of techniques that use VOC measurements and meteorological data in conjunction with a form of the Gaussian dispersion equation to estimate the emission rate<sup>3</sup>.

The study is divided into three phases, which consist of field testing the emission rate models using only a single point source during Phase 1, using multiple point sources to simulate an area source during Phase 2, and at selected actual VOC area and/or point sources during Phase 3. The three phases are being performed consecutively over a three-year period.

The objectives of the study include the following: (1) the development of field protocols to ensure that data collected will be of appropriate type and quality to perform emission rate estimations; (2) an assessment of the performance of the emission rate models for both the single-point-source and area-source cases, including a determination of statistically appropriate confidence intervals; (3) a determination of the applicability and relative accuracy of the models as a function of downwind distance and atmospheric stability; and (4) a determination of the effect of VOCs being released at different heights within an area source.

Data collection for Phase 1 is scheduled to be completed in June, 1993. Data collected through November, 1992, are reported and analyzed in this paper. Because of space constraints, only results obtained for 1,1,1-trichloroethane (1,1,1-TCA) are interpreted and discussed in detail in this paper. Results for other compounds are summarized here and discussed in more detail elsewhere<sup>4,5</sup>.

### MODEL DESCRIPTION

Two emission rate models are being evaluated for the single-point-source case in Phase 1. Both models are based on the premise that integration of the Gaussian dispersion equation in the crosswind direction results in an expression for the emission rate as a function of the path-integrated concentration<sup>3</sup>. The models differ in their use of meteorological data: Model 1 uses values for wind speed and wind direction that are averaged over the duration of the test period; Model 2 employs one-minute means of those variables<sup>6</sup>. Other models, or modifications of the above models, will also be evaluated should the results warrant that action.

Justification for using one-minute means of meteorological data in an emission rate model is provided in a previous study, in which meteorological data were used to estimate the crosswind distribution of material within a VOC plume<sup>6</sup>. Based on the results of that study, the use of one-minute means yields a significant improvement in estimating both the shape of the concentration-versus-crosswind distance curve and the magnitude and location of the highest concentrations, when compared to the use of meteorological data averaged over the entire test period.

During Phase 1, the effective emission height and the measurement height are both approximately two meters. With the source and receptors very near ground level, the applicable form of the Gaussian dispersion equation is as follows<sup>7,8</sup>:

$$C(x,y) = (Q/\pi\sigma_y\sigma_z)\exp[-1/2(y/\sigma_y)^2], \quad (\text{Equation 1})$$

where  $C(x,y)$  = concentration at  $(x,y)$ , in  $\text{mg}/\text{m}^3$ ,  
 $Q$  = emission rate, in  $\text{mg}/\text{sec}$ ,  
 $\sigma_y, \sigma_z$  = horizontal and vertical dispersion coefficients, in  $\text{m}$ ,  
 $u$  = mean wind speed, in  $\text{m}/\text{sec}$ , and  
 $x, y$  = downwind and crosswind distances to receptor, in  $\text{m}$ .

Integrating with respect to  $y$ , from  $y = -\infty$  to  $y = +\infty$ , and rearranging yields

$$Q = [(2\pi)^{1/2}C_y\sigma_y u], \quad (\text{Equation 2})$$

where  $C_y$  = crosswind path-integrated concentration, in  $\text{mg}/\text{m}^2$ .

This method should produce a reasonably accurate value for the emission rate, given an accurate value of the crosswind path-integrated concentration and the satisfaction of assumptions made in the development of the above equations.

The assumptions used in developing the Gaussian equation (Equation 1) are seldom rigorously adhered to in field tests. However, various sensitivity analyses show that meeting some assumptions is more critical than others. For example, over short diffusion times (approximately one minute) and within small distances (the first tens of meters), the downwind distribution of material should take the same form as the wind-fluctuation distribution, which approximates a Gaussian distribution fairly closely<sup>9,10</sup>. In addition, although the assumption of a Gaussian vertical profile is often deviated from, especially under convective conditions, deviations are not so serious that it fails as a working assumption<sup>9</sup>.

Equation 1 was integrated with respect to  $y$  to derive Equation 2. This operation involved an assumption that  $x$  (and, consequently,  $\sigma_y$  and  $\sigma_z$ ) was held constant. Therefore, the path-integrated concentration must be determined for a

path normal to the mean wind direction. In addition, the integration was from  $-\infty$  to  $+\infty$ ; thus, all of the plume constituents at the measurement height must pass within the boundaries of the sampling network. Because of fluctuating winds, those assumptions are often violated, and in those cases the direct application of Equation 2 will not yield an accurate emission rate.

The models described in this paper attempt to overcome this problem by using meteorological data to characterize the configuration of the plume during the test period, allowing Equation 2 to be used more accurately. Consider Equation 1 in a rewritten form:

$$Cu/Q = (1/\pi\sigma_y\sigma_z) \exp[-1/2(y/\sigma_y)^2]$$

Summation of Cu/Q values for evenly spaced points along the measurement path yields a relationship between path-integrated concentration, wind speed, and emission rate for a given stability class and sampling network orientation:

$$\Sigma\{(1/\pi\sigma_y\sigma_z) \exp[-1/2(y/\sigma_y)^2]\}/n = \Sigma(Cu/Q)/n \approx C_yu/Q$$

Values for  $C_yu/Q$  can be calculated under the ideal-case conditions used to derive Equation 2 and summed across the path to yield  $(C_yu/Q)_i$ . Values can also be calculated using the measured wind direction data from the test period and summed to yield  $(C_yu/Q)_M$ .

The ratio of these two values can be used as follows:  $C_{y_i} = C_{y_M} (C_yu/Q)_i / (C_yu/Q)_M$

where  $C_{y_i}$  is the path-integrated concentration that would be observed under the ideal-case conditions and  $C_{y_M}$  is the measured path-integrated concentration.  $C_{y_i}$  can then be used in Equation 2 to more accurately estimate the emission rate.  $(C_yu/Q)_M$  can be determined either by using means of wind speed and wind direction for the entire test period, or by using one-minute means of those variables. These two methods of determining  $(C_yu/Q)_M$  give rise to the two emission rate models alluded to previously<sup>4</sup>.

Dispersion coefficients ( $\sigma_y$  and  $\sigma_z$ ) were determined from Pasquill-Gifford stability classifications, which were estimated from the standard deviation of the horizontal wind direction ( $\sigma_\theta$ ). It is likely that  $\sigma_y$  and  $\sigma_z$  can be more accurately determined by other methods. One such method is the use of a tracer to develop site-specific coefficients. Another method is to determine  $\sigma_y$  and  $\sigma_z$  by relating them directly to the measured deviations of horizontal and vertical wind directions ( $\sigma_\theta$  and  $\sigma_\phi$ )<sup>8</sup>. Prior to May, 1992,  $\sigma_\phi$  was not measured. Since that time, however, measurements of both  $\sigma_\theta$  and  $\sigma_\phi$  are being made. This method of determining  $\sigma_y$  and  $\sigma_z$  is undergoing refinement and will be incorporated into a third model.

## EXPERIMENTAL METHODS

Because of space constraints, a detailed methodological description, in terms of study site characteristics, VOC plume generator capabilities, meteorological data collection, and VOC sampling and measurement protocol, is not given here, but is available elsewhere<sup>4,5</sup>. A discussion of the Phase 1 data requirements is given in the following paragraphs.

In order to meet the objectives of Phase 1 of the study, data must be collected at several downwind distances, and under a variety of stability conditions. The minimum downwind distance of 50 meters allows a relatively steady-state plume to develop prior to reaching the sampling network, while still providing measurable concentrations. Maximum downwind distance will be no more than 250 meters, although this distance is dependent on results obtained at lesser distances. The dimensions of the sampling network are adjusted along with downwind distance in an attempt to place a large percentage of the plume within the path during as many test runs as possible. Although the choice of sampling days provides a generally similar synoptic weather framework from test day to test day (relatively steady winds at approximately 2-5 m/s, and no frontal passage or precipitation), the effect of stability on the testing regime can be examined by selecting the timing of test periods within a given day.

In order to evaluate the validity of the estimation methods over a wide range of emission rates, this parameter is varied from test to test. Triplicate releases of six different mixtures of two compounds are normally conducted during each test day. The composition of the mixtures and the flow rate into the plume generator are varied so that emission rates of each compound span the range of 20-200 ml/min (liquid flow rate).

## RESULTS AND DISCUSSION

Data collected through November, 1992 (including the Intercomparison Study of 1991<sup>11</sup>) have been used to evaluate the emission rate models described here. Overall results for all compounds released are summarized in Figures 1 & 2; because of space constraints, more detailed analyses, as shown in Figures 3-7, are restricted to results obtained for 1,1,1-TCA. A more complete presentation of the results is given elsewhere<sup>5</sup>.

Overall performance of Equation 2, Model 1, and Model 2 for 1,1,1-TCA, toluene, and for a third data set that includes all other compounds released, is shown in Figure 1. Results displayed in Figure 1 are based on canister-derived path-integrated concentrations, as generated using a previously developed technique<sup>6</sup>. Estimation accuracy is expressed as a percentage of the measured emission rate. Prior to calculating the mean accuracies plotted in Figure 1, outliers were removed from the data set according to a method by Dixon<sup>12</sup>. Based on the values shown, Model 1 provides a slight increase in estimation accuracy over Equation 2; an additional increase in accuracy is provided by Model 2. Slightly better estimation accuracies are seen for toluene than for the other compounds.

Overall performance of Equation 2, Model 1, and Model 2, as based on FTIR measurements, is shown in Figure 2. Results are similar to those obtained from canister data, although FTIR estimation accuracy is slightly lower for 1,1,1-TCA and toluene, and slightly higher for other compounds.

The sensitivity of the models to atmospheric stability can be explored by examining Figures 3 and 4, which show mean estimation accuracies for tests conducted under class B, C, and D stability conditions. Results indicate that model accuracy for 1,1,1-TCA is better for tests conducted under class B stability conditions than for those conducted under more stable conditions. In addition, Model 2 provides increased accuracy over Model 1 as conditions become more unstable.

Through November, 1992, data were collected at three downwind distances to investigate the influence of this variable on the emission rate determination. Figure 5, based on canister data, shows that model performance is better at 100 and 150 meters than at 50 meters. Model 1 provides a significant increase in model accuracy over the direct application of Equation 2 at 150 meters; Model 2 provides an additional significant increase in accuracy. Less difference among the mean estimation accuracies for the three methods is observed at 50 and 100 meters. Figure 6, based on FTIR data, shows a slight improvement at 100 meters over 50 meters; note that no FTIR data has been collected at 150 meters.

Analyses of variance were performed in an attempt to provide additional insight into the effects of stability and downwind distance on each of the estimation methods. Results of these analyses indicated the following: (1) all three methods show greater sensitivity to stability than to distance, (2) a small contribution to the variation is made by the interaction of stability and distance; and (3) Model 2 is more sensitive to both stability and distance than are Equation 2 or Model 1. The fact that stability, distance, and the interaction between the two variables all contribute to the variation observed implies that caution must be used in making general conclusions about model sensitivity based on the limited data set thus far collected.

Equation 2 was derived using the following two assumptions: (1) the path-integrated concentration must be determined for a path normal to the mean wind direction; and (2) all of the plume constituents at the measurement height must pass within the boundaries of the sampling network. In cases where those assumptions are violated, the direct application of Equation 2 will not yield an accurate emission rate. Model 1 and Model 2 are being evaluated during Phase 1 of this study to determine the extent to which this problem can be overcome through the use of meteorological data. Therefore, it would be informative to look more closely at those tests in which one or both of the underlying assumptions were violated. The overall performance of the estimation methods for those tests is shown in Figure 7 for 1,1,1-TCA. (Note that Assumption 1 was considered to be violated if the mean wind direction was 15 degrees or more different from the network centerline direction. Assumption 2 was considered to be violated if less than 95% of the plume constituents at the measurement height passed within the sampling network, based on the meteorological data.)

As seen in Figure 7, Model 1 provides a significant increase in mean estimation accuracy over the direct application of Equation 2. Model 2 provides a significant additional increase, its mean estimation accuracy being approximately 17% greater than that of Equation 2 for canister results (approximately 15% greater for FTIR results). In addition, Model 2 provides large increases in estimation accuracy for a number of individual tests<sup>5</sup>. Therefore, results indicate that the use of meteorological data in the models described in this paper allows Equation 2 to be applied more accurately in cases where its underlying assumptions are violated. Furthermore, the use of one-minute means of meteorological data (as in Model 2) provides a significantly greater increase in estimation accuracy than does the use of meteorological data that are averaged over the entire test period (as in Model 1).

## CONCLUSIONS

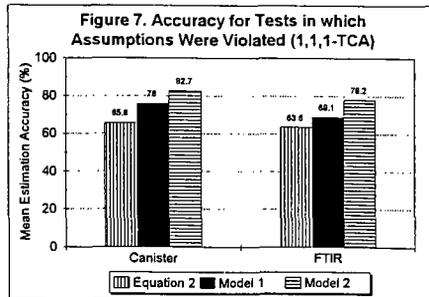
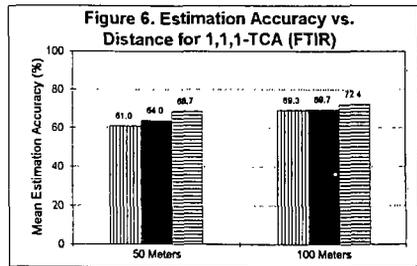
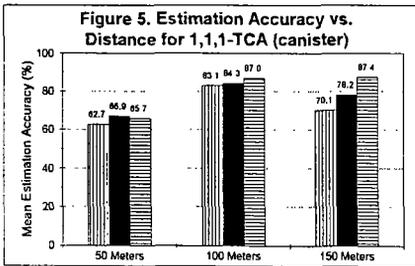
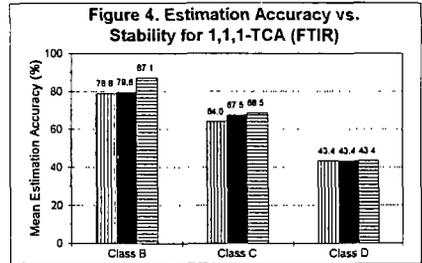
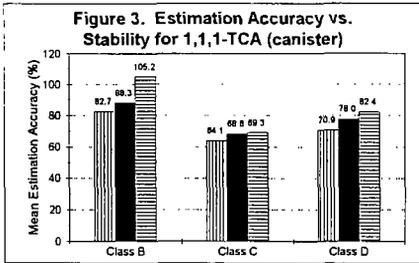
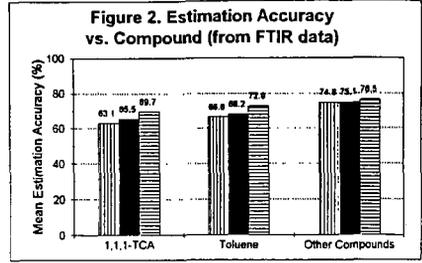
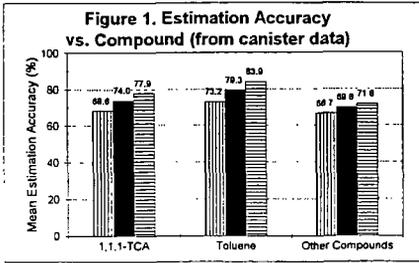
During Phase 1 of this study, two models that estimate VOC emission rate from a single point source, using path-integrated concentrations and meteorological data, are being evaluated. The performance of Model 1 (which uses meteorological data that are averaged over the entire test period) and Model 2 (which uses one-minute means of

meteorological data) are compared to the direct application of Equation 2 (the integrated Gaussian dispersion equation). The sensitivity of the models to atmospheric stability and downwind distance is also being evaluated. Results analyzed in this paper produce the following conclusions:

1. Based on data from all tests, Model 1 provides an increase in emission rate estimation accuracy over the direct application of Equation 2. Model 2 provides a slight additional increase in accuracy.
2. Based on data from only those tests during which the assumptions used to derive Equation 2 were violated, Model 1 provides a significant increase in estimation accuracy; Model 2 provides a significant additional increase. Therefore, the models described in this paper allow Equation 2 to be applied more accurately in cases where its underlying assumptions are violated.
3. Estimation accuracy is better for tests conducted under class B stability conditions than for those conducted under more stable conditions. Model 2 provides increased accuracy over Model 1 as conditions become more unstable.
4. Model performance is better at 100 and 150 meters downwind distance than at 50 meters. Model 1 provides a significant improvement over the direct application of Equation 2 at 150 meters; Model 2 provides a significant additional improvement. Much less difference among the estimation methods is observed at 50 and 100 meters.

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**Ambient Air Monitoring Siting Criteria for Open Path Analyzers  
Measuring Nitrogen Dioxide, Ozone, and Sulfur Dioxide.**

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**ABSTRACT**

Open path analyzers using ultraviolet spectroscopy are commercially available as ambient air monitoring instruments. Definitive siting criteria would be needed in order to incorporate these instruments into the State and local ambient air monitoring networks. This paper explores the issues involved with establishing siting criteria and discusses proposed criteria which parallel existing requirements for conventional analyzers. Specifically, this paper discusses open path monitor siting for nitrogen dioxide, ozone, and sulfur dioxide (the three pollutants which are measurable by ultraviolet-based open path analyzers) that also have National Ambient Air Quality Standards.

## INTRODUCTION

A new method for monitoring pollutants in ambient air has been developed and introduced to the ambient air monitoring community.<sup>1</sup> This new monitor is a type of open path analyzer that is referred to as a differential optical absorption spectrometer (DOAS). The DOAS uses an ultraviolet light beam to measure atmospheric pollutant concentrations in situ over a path of several meters up to several kilometers. In contrast, traditional monitoring methods, or "fixed point analyzers", measure gaseous pollutant concentrations by extracting a sample of air from the atmosphere through an inlet probe.

A major regulatory use for ambient air monitoring data is for comparison of measured concentrations against the National Ambient Air Quality Standards (NAAQS). The NAAQS define levels of air quality which have been determined by the U.S.EPA as necessary to protect public health and welfare from adverse effects from exposure to specific air pollutants.<sup>2</sup> Six air pollutants, often referred to as the "criteria pollutants", currently have established NAAQS. The criteria pollutants are ozone, nitrogen dioxide, sulfur dioxide, carbon monoxide, lead, and particulate matter (PM-10). Of these six pollutants, ozone, nitrogen dioxide, and sulfur dioxide are measurable by open path analyzers using ultraviolet based spectroscopy.<sup>3</sup>

In order for open path ambient air monitoring data to be used for regulatory purposes, appropriate siting criteria must be developed for these instruments and included in the appropriate regulation. Designing these criteria in a way that they parallel the existing requirements for fixed point monitors would be prudent to ensure that the open path data would be compatible with the existing State and local air monitoring data bases. This paper will discuss potential siting criteria for the DOAS analyzers for measuring ozone, sulfur dioxide, and nitrogen dioxide.

## SITING CRITERIA DESIGN

The existing ambient air monitor siting requirements are defined within the air quality surveillance regulations in terms of monitoring objectives and geographic area, or "spatial scale of representativeness".<sup>4</sup> The four basic monitoring objectives for a given area are to determine maximum concentrations, population exposure, specific source impact, and background concentrations. The geographic location of each monitoring station within this area is dependent upon the monitoring objective for that site. To clarify this link between matching a monitoring objective with the appropriate geographic location, the concept of spatial scale of representativeness, or measurement scale, is introduced. Spatial scales of representativeness are defined in terms of the physical dimensions of the atmospheric volume to be represented by a monitoring station. It is assumed that the pollutant concentrations are reasonably homogeneous throughout this air volume; therefore, a point monitor placed within this air volume would produce concentrations representative of that measurement scale, provided that the monitor were sited according to specific criteria.

Six measurement scales, with their associated physical dimensions, are defined in the regulations. Of these six scales, four are listed in the regulation as normally associated with ambient air monitoring of ozone, nitrogen dioxide, and sulfur dioxide. These scales are described as middle scale, neighborhood scale, urban scale, and regional scale. Figure 1 illustrates the measurement scales used most frequently by the State and local air monitoring programs.<sup>5</sup> Those measurement scales which are used to monitor ozone, nitrogen dioxide, and sulfur dioxide are identified on Figure 1 beneath the measurement scale dimensions. For the majority of existing ozone and nitrogen dioxide monitoring applications, the scales of representativeness are neighborhood or urban scale. Both ozone and nitrogen dioxide are photochemically formed, rather than emitted directly from local sources, and their concentration gradients tend to be more homogeneous and better represented by the larger scales of measurement. Sulfur dioxide emissions are predominantly from large point sources; therefore, sulfur dioxide ambient air monitoring is usually conducted on the smaller scales, particularly middle and neighborhood scales.

Assuming that the pollutant concentration within a particular measurement scale is nearly homogeneous, it would seem that a path integrated measurement taken within the dimensions of that measurement scale would provide a concentration descriptive of that area of interest. Open path analyzers appear to provide a more spatially representative measurement than traditional, fixed point methods because of their inherent path integration measurement capabilities. Conversely, this spatial averaging technique may not be advantageous when significant nonhomogeneities exist within a given air mass and the monitoring objective is to obtain the maximum concentration at a certain point. This trade-off between capturing maximum pollutant concentrations at a point and measuring spatially averaged concentrations is a fundamental difference between point and open path technologies. This difference should be considered when choosing the monitoring technology for application in areas with significant concentration inhomogeneities.

To ensure that an open path monitor would collect data that is representative of the intended monitoring objective, specific path siting criteria would be needed. These new criteria should be designed to achieve the same objectives as the current requirements in order to allow the use of open path data interchangeably with point data within the same monitoring network. The existing criteria<sup>6</sup> could be adapted to accomplish this task. For ozone, nitrogen dioxide, and sulfur dioxide monitoring, these criteria could be written based on the following siting considerations, which are analogous to current regulations.

#### **Definition of "Path"**

The definition of "path" used within these criteria is the actual path in space through which the analyzer measurement beam passes and over which the pollutant concentration is measured and averaged. This definition of "path" may differ from the optical path length used by the analyzer to calculate the path averaged concentration. The optical path length would be described as the total distance the light beam travels between the transmitter and the receiver. (For example, when a retroreflector is used, the optical path length is the distance from the transmitter to the retroreflector plus the distance from the retroreflector to the receiver.)

#### **Horizontal and Vertical Path Placement**

For ozone, sulfur dioxide, and nitrogen dioxide fixed-point analyzers, current regulations require that a monitoring probe be located 3 to 15 meters above ground. The corresponding height above ground requirement for open path analyzers could require that 80% of the path must meet the 3 to 15 meters above ground criteria. Similarly, in regard to the horizontal and vertical distance from the path to any supporting structure, the criterion for open path analyzers could be that 90% of the total path must be one meter, horizontally or vertically, away from any supporting structure.

#### **Spacing from Minor Sources**

The proposed siting criterion which addresses distancing the path from minor sources would be similar to the current requirements. For ozone open path analyzers, at least 90% of the path should be away from minor sources of nitrogen oxides. Similarly, 90% of the path used to measure sulfur dioxide should be away from minor sources of sulfur dioxide, such as furnace or incineration flues.

#### **Spacing from Obstructions**

This criterion applies for any open path analyzer, regardless of the pollutant measured. Any path must be clear of all trees, brush, buildings, plumes, dust, or other optical obstructions, including potential obstructions that may move due to human activity, wind, or growth of vegetation. This criteria is especially important for open path analyzers because of their optical requirements. Also, at least 90% of the path should have unrestricted airflow and be located away from buildings and other obstacles. Obstacles would be defined as any building, tree, or other object that protrudes above the path at a height greater than or equal to half the horizontal distance from the path to the object.

#### **Spacing from Trees**

Trees can provide surfaces for adsorption of ozone, nitrogen dioxide, and sulfur dioxide, and they can obstruct wind flow. To reduce interference from trees, 90% of the path must be 10 meters or more from the drip line of trees or brush. Additionally, for any tree(s) that may be considered an obstruction, the path must meet the "Spacing from Obstructions" requirements listed previously.

#### **Spacing from Roadways**

Due to the reactive nature of ozone and nitrogen dioxide when combined with mobile source emissions, certain limits must be placed on paths that are in the vicinity of roadways or similar heavily trafficked areas. It would be preferable if the path did not cross any roadway; however, practical siting conditions make this seem unrealistic. Most ozone and nitrogen dioxide monitors would be placed in areas with small, lightly traveled residential streets in rural or suburban areas. A more practical requirement would be to allow a path to cross a roadway with an average daily traffic count of 10,000 or fewer vehicles per day.

Additionally, some consideration should be given to paths in close proximity to larger roadways. Table 1 lists

the minimum separation distances between roadways and probes as they are defined in existing regulation. These minimum separation distances, which vary in size with traffic count, are used to limit the probe's siting within the "area of potential interference" from vehicle emissions. Similarly, for open path analyzers, it is reasonable to assume that a portion of the path, while not wholly crossing a roadway of greater than 10,000 vehicles per day, could be located closer to a major roadway than the minimum separation distance. A criterion to limit this interference would be that 90% of any path must meet the same minimum separation distances specified for fixed point monitoring probes located near a roadway. This criterion would be included in addition to the limitation that a path must not cross a roadway with greater than 10,000 vehicles per day.

**Table 1. Minimum separation distance between neighborhood & urban scale ozone & nitrogen dioxide probes & roadways\***

Roadway average daily traffic, vehicles per day	Minimum separation distance between roadways & probes (meters)
≤ 10,000	10
15,000	20
20,000	30
40,000	50
70,000	100
≥ 100,000	250

\*Distances should be interpolated based on traffic flow.

### Cumulative Interferences on Path

Some consideration should be given toward controlling the combined total affect on a path measurement from all the possible interferences which exist around the path. To control the sum effect of these interferences, a requirement could state that the cumulative length of a path that is affected by minor sources, obstructions, trees, and roadways must not exceed 10% of the path. Figure 2 illustrates this concept. In this example, an open path analyzer is sited with two interferences, a tree and a roadway with an average daily traffic count of less than 10,000 vehicles per day. To calculate the portion of the path affected by the tree, it is necessary to determine how much of the path would be obstructed by the tree from the predominant wind flow. This portion is labeled as "Z" on Figure 2. To determine the portion of the path affected by the roadway, it is necessary to sum the length of the path segments over the roadway with those over the minimum separation distance on both sides of the roadway, defined by "x" on Figure 2. This portion of the path is labeled as "Y". The sum of "Z" and "Y" is the total interference on this path. It is this sum which must be less than 10% of the total path.

### Maximum Length of Path

Since the measurement scales are defined in terms of finite physical dimensions, some consideration must be given to the maximum length of a path used to monitor within each of these measurement scales. For ozone, nitrogen dioxide, and sulfur dioxide analyzers measuring concentrations based on neighborhood, urban, or regional scales, the maximum path length could be one kilometer. For middle scale measurements of these three pollutants, a maximum path length of 300 meters may be appropriate. These path limitations are necessary in order to produce a path concentration representative of the measurement scale and to limit the averaging of peak concentration values.

In actual siting situations, some slight deviations from these criteria may be necessary to account for actual siting conditions. Consequently, the waiver provisions allowed for probe siting should also apply for open path analyzers. Future refinement of these criteria would be possible as monitoring agencies gain more experience from using the DOAS and other open path analyzers.

### CONCLUSIONS

Each monitoring station has an associated monitoring objective and spatial scale of representativeness, or measurement scale. Given that the appropriate measurement scales for monitoring ozone, nitrogen dioxide, and sulfur dioxide will range in dimensions from 100 meters to more than 50 kilometers, it is reasonable to state that open path analyzers would be able to measure pollutant concentrations representative of each of these scales. Specific path siting

criteria would be needed to limit path interferences which would cause the analyzer to produce unrepresentative data. These criteria should be stringent enough to cause the open path analyzers to produce data that would be useful for the protection of public health, while also remaining flexible enough to encourage the use of this technology.

## DISCLAIMER

The information within this document has been subjected to review by the United States Environmental Protection Agency and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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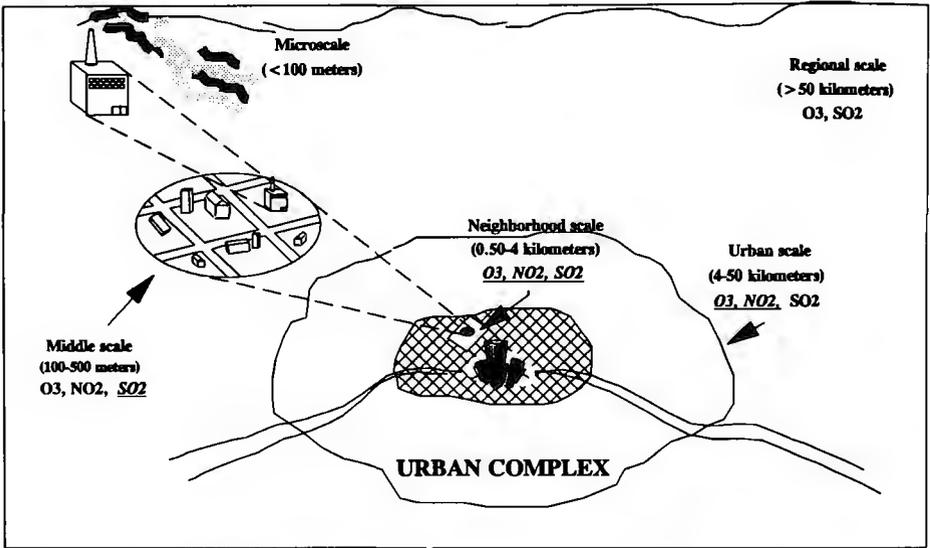


Figure 1 Measurement scales for ambient air monitoring.  
 (See reference 5 - Ball and Anderson)

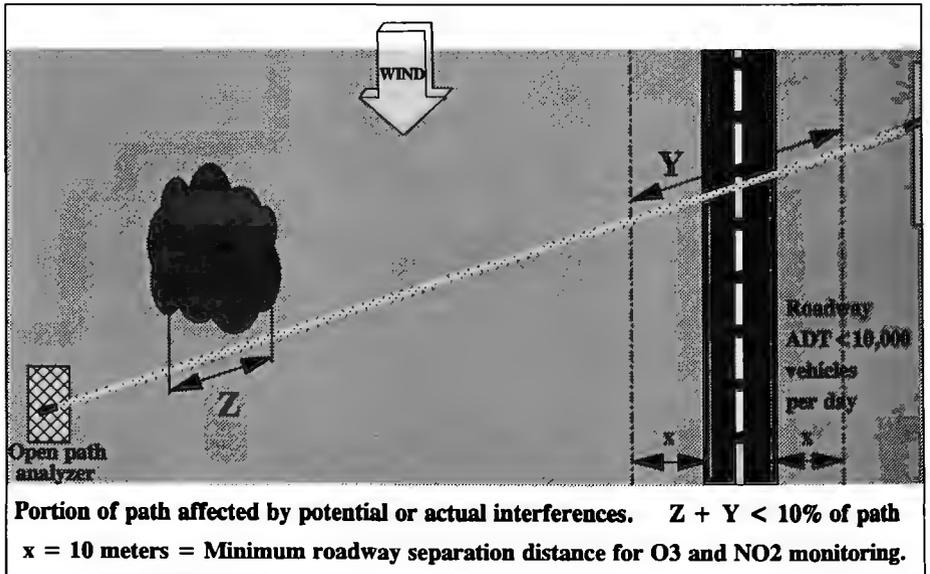


Figure 2 Example of cumulative effects on path.

## MONITORING FOR FUGITIVE EMISSIONS AT SUPERFUND SITES DURING REMEDIATION ACTIVITIES WITH AN FTIR REMOTE SENSOR

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### INTRODUCTION

An FTIR remote sensor (FTIR-RS) was used to monitor for fugitive emissions during remediation activities at several contaminated sites. These include the Lapari Landfill Superfund site in south New Jersey, the Gulf Coast Vacuum Superfund site in Louisiana, the Westminster Superfund site in Orange County, California, and a 17 acre surface impoundment which will undergo remediation by removal and solidification. The FTIR measurements were used in a plume dispersion model to calculate the emission rates of toxic gases and the downwind impact in areas of human activity.

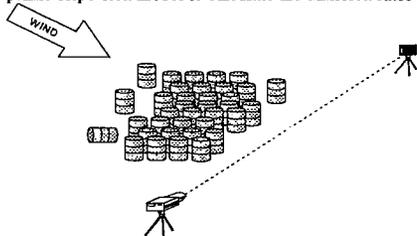


Figure 1

The FTIR Remote Sensing System. The FTIR-RS uses a single telescope to both transmit a 12 inch collimated infrared beam to the atmosphere, and receive the infrared beam after it traversed a round-trip path through the atmosphere. A 14 inch corner-cube retroreflector array is used to reverse the path of the ir beam back to the transmitter / receiver telescope.

A recent review describes the use of optical remote sensors, including the FTIR-RS, to measure toxic gases.<sup>1</sup> The FTIR-RS used in the present programs was designed as a unistatic design which uses a single transmitter/receiver telescope. Figure 1 shows a simple schematic of the measurement setup. The infrared radiation is modulated by a Michelson interferometer, of a wishbone design, which uses corner-cube retroreflectors. This retroreflector-interferometer design eliminates the need to make field alignment adjustments on the interferometer, with changing temperature. The modulated infrared radiation is collimated by a 12 inch cassegrain telescope and transmitted through the parcel of atmosphere being measured to a corner-cube retroreflector array. The array reflects the beam back to the single transmitter/receiver telescope, resulting in two passes through the chemical plume. The radiation is then focused on the aperture of a mercury cadmium telluride (MCT) detector. The modulated signal, referred to as an interferogram, is Fourier transformed to produce a spectrum from  $700\text{ cm}^{-1}$  to  $4500\text{ cm}^{-1}$ , with  $1\text{ cm}^{-1}$  resolution. This system was designed with the primary goal of fast and easy setup and alignment. This is particularly important in Superfund and similar applications involving very contaminated areas. The system can be setup in a matter of minutes. The retroreflector array's orientation is not critical for proper alignment, so if it needs to be setup in a restricted, highly contaminated area by personnel in protective garments, it takes only a few seconds to set down and to orient so as to face (within 10 degrees) in the direction of the telescope.

The FTIR-RS is particularly well suited for monitoring for fugitive chemical emissions during remediation activities to provide emergency response. These systems can detect and measure the concentrations of a multitude of infrared absorbing gaseous chemicals in real-time. The conventional Summa canister sampling methods require the subsequent analysis, usually by gas chromatography / mass spectrometry (GC / MS). This process is too slow for canister collection techniques to be of use for emergency response. The FTIR-RS and other optical remote sensors measure concentrations over an integrated path. This type of measurement is extremely useful as an input to a plume dispersion model to calculate emission rates. If the FTIR-RS measurement is made in the crosswind direction, covering the entire distribution in that direction, the only dispersion of concern is in the vertical direction. This greatly simplifies the dispersion analysis. Another advantage of the FTIR-RS technique is that it is an *in-situ* measurement and is therefore not affected by wall adsorption effects that occur in collection or extraction systems; the FTIR-RS can directly measure polar molecules.

### FTIR MEASUREMENTS

The FTIR-RS is used to make integrated-path concentration determinations of the chemical constituents in a plume.

The infrared beam path is set up in the crosswind direction, downwind of the emission source, with the end points chosen so that the entire plume crosses the beam path. These measurements made downwind of the emission source are referred to a downwind measurements. The initial spectroscopic data are single beam spectra,  $I$ . According to Beer's law, the concentration-pathlength product,  $CL$ , of an absorbing chemical is proportional to the absorbance,  $A$ , which is defined as

$$A(\nu) = -\log ( I(\nu) / I_0(\nu) ), \quad (1)$$

where all three quantities here are spectra and are written as functions of  $\nu$ , the optical frequency in wave number ( $\text{cm}^{-1}$ ) units.  $I_0(\nu)$  is the background spectrum taken under identical conditions to  $I(\nu)$ , with the exception that the absorbing chemicals are not present. Beer's law is written as

$$A(\nu) = \epsilon(\nu) CL, \quad (2)$$

where the proportionality constant,  $\epsilon(\nu)$  is the absorption coefficient of the chemical. The absorption coefficient is essentially a spectral shape function and is unique for each molecule, resulting in the unique "fingerprint" shape of the chemical absorption spectrum used in making qualitative identifications. The quantitative determination is made by measuring the absorbance,  $A(\nu)$ , and determining the concentration-pathlength product,  $CL$ , of the absorbing chemical.

The concentration-pathlength products of the absorbing chemicals are calculated using the multicomponent classical least-squares technique (CLS) developed by Haaland and Easterling.<sup>2</sup> This technique involves performing a least-squares fit of the field spectra to reference spectra (of the absorbing chemical species) using Beer's law,

$$A_S(\nu) = a + b \nu + \sum_r \gamma_r A_r(\nu) + e(\nu), \quad (3)$$

where  $A_S(\nu)$  is the total absorbance of the measured atmospheric spectrum, at frequency  $\nu$ ,  $A_r(\nu)$  is the absorbance of the  $r$ th reference spectrum and  $\gamma_r$  is the ratio of the concentration-pathlength product for the  $r$ th chemical in the field, to the concentration-pathlength product for the reference spectrum of the  $r$ th chemical. The first two terms, on the right side of the equation, perform a linear correction for baseline error. The range of frequencies,  $\nu$ , for the analysis are limited to regions where the target compound actually absorb the radiation. For each region, the sum in the third term is over all species which absorb in that particular region. The last term is the error or residual of the fit. The reference spectra are measurements of the pure gases, usually mixed in one atmosphere of dry air or nitrogen.

#### EMISSION RATE DETERMINATION

A Gaussian plume dispersion model was used primarily to determine the emission rates of the toxic gases from the FTIR-RS measurement. The determined emission rates are then used in the dispersion model to calculate the concentrations at fences lines and at points where human activity occurs. The emission rates were determined from the FTIR-RS measurements by two different methods, the tracer ratio technique and by plume dispersion calculation using site-specific coefficients for the dispersion in the vertical direction,  $\sigma_z$ . When the path integrated concentration measurement path is in the crosswind direction and the height of the measurement is the same as the height of the emission source, the general Gaussian dispersion equation (Turner Equation) for the emission rate,  $Q_a$  simplifies to

$$Q_a = \sqrt{\pi/2} (CL)_a \sigma_z U_x, \quad (4)$$

where the index,  $a$ , refers to a particular gaseous chemical,  $(CL)_a$  is the ground-level crosswind-integrated concentration-pathlength product (path-integrated concentration), in grams / meter<sup>2</sup>, measured at distance  $x$  from the emission source, for chemical,  $a$ , and  $U_x$  is the horizontal wind speed in meters per second.

The tracer ratio technique involves releasing a tracer gas,  $t$ , (usually carbon tetrafluoride or sulfur hexafluoride) with a measured emission rate,  $Q_t$ , and measuring the tracers concentration-pathlength product,  $(CL)_t$ , with the FTIR-RS, at distance  $x$  from the source. Using Eq (4), the emission rate for unknown chemical emission  $a$ ,  $Q_a$ , can be written as

$$Q_a = [ (CL)_a / (CL)_t ] Q_t. \quad (5)$$

Thus, the problem reduces to emitting the tracer with a known emission rate and measuring  $(CL)_t$  simultaneously with the concentration-pathlength products for the emitted chemicals.

The second method of determining emission rates is to use site specific values for the vertical dispersion coefficient,  $\sigma_z$ , along with the wind speed,  $U_x$ , in Eq (2). In cases where the measurement configuration do not satisfy the requirements for using Eq (2), one uses the general plume dispersion expression, the Turner equation.

#### THE SITE MEASUREMENT CONFIGURATIONS

Figure 2 shows examples of the FTIR-RS setup configurations used at the four contaminated sites. Figure 2a shows the Lapari Landfill Superfund Site in south New Jersey. This site contains hazardous liquid contaminants in the soil, which could migrate to the ground water. The remediation involves drilling wells into landfill cells, and pumping water into them to displace the buried the contaminants. The hazardous contaminants are carried through ground water pathways to interception wells dug at the periphery of the site. The contaminated water in the interception wells were pumped out, to prevent the contamination from leaving the site in the ground water, and directed to a water treatment facility. The treated water was then recycled back to the wells in the landfill cells. This flushing procedure continues until the contaminants are reduced to safe levels. This procedure, and activities such as drilling monitoring wells to obtain ground samples, could result in the volatilization of the organic contaminants producing air toxics. The FTIR-RS monitored for air toxics during these activities. Figure 2a shows the FTIR measurement configuration used to monitor for air toxics during the drilling of Well No. 22. The direction of the wind would carry any resulting emission plume across the infrared beam. The position of the meteorological tower was located upwind of the infrared beam. The vertical dispersion coefficient,  $\sigma_z$ , was estimated from site specific tracer measurements, and the emission rate was calculated using Eq (4). The distance between the FTIR sensor and the retroreflector array was 100 meters.

Figure 2b shows the configuration at the Gulf Coast Superfund site in Abbeville, Louisiana. At this site, the soil was contaminated by the petroleum wastes which resulted from past oil drilling operations. The FTIR-RS was introduced for a pilot scale remediation study to determine the impact on air quality during the various test remediation procedures. The air emission rates were measured during sludge excavation activities and during the process of solidifying the sludge. The latter process produces heat which could drive off the more volatile components of the contamination. Figure 2b shows the FTIR-RS measurement configuration during sludge excavation. The wind here had two prevailing directions (from the Gulf of Mexico and from the north) and tended to shift from one to the other, so we used a folded beam configuration to intercept the plume regardless of the wind direction. In this configuration, the tracer gas was released at the excavation site and the ratio method of determining the emission rate (see Eq (5)) was used. The distance from the FTIR sensor to the mirror was 60 meters and the total round trip beam path was 240 meters.

Figure 2c shows the configuration at the Westminster Superfund site in Orange County, California where another pilot scale program evaluated the FTIR-RS for measuring emission rates during excavations. A folded beam path was used to double the passes through the plume, resulting in four passes, round trip (transmitter/receiver telescope to the retroreflector array and back). The tracer gas was released at the excavation site and the ratio method, to determine the emission rate, was used. The distance from the FTIR sensor to the mirror was 32 meters and the total beam path was 128 meters. Figure 2d shows the configuration used at the surface impoundment / RCRA application. The FTIR measurements were made during sludge dredging activity. The distance between the FTIR sensor and the retroreflector array was 175 meters.

#### THE MEASUREMENT RESULTS

Two examples of FTIR-RS spectra are shown in Figure 3. Figure 3a shows a field spectrum obtained at the Gulf Coast Superfund site (upper trace). The middle trace is the laboratory-measured reference spectrum for n-octane (500 ppm-meter) and the lower trace is the reference spectrum for methane (81 ppm meter). Aliphatics higher than C-8 were present at the Gulf Coast site, however, their spectra are similar to octane. The octane reference is used to represent the aliphatics, C8 and higher. Since octane is the most volatile of these, it is expected to be the most predominant component.

A comparison of a field spectrum taken at the Westminster Superfund site to the reference spectrum of sulfur dioxide is shown in Figure 3b. The upper trace is the field spectrum and the lower trace is the reference spectrum for sulfur dioxide (476 ppm meter). A determination of 48.2 ppm meters of sulfur dioxide was made from this field spectrum. The total round-trip pathlength was 128 meters, thus the path averaged concentration was 377 ppb. This determination, with the measured wind speed, and a carbon tetrafluoride tracer determination, resulted in an emission rate value of 0.80 g / sec for sulfur dioxide.

Examples of the FTIR-RS / Plume Dispersion Model measurement results are shown in Tables 1 to 4. Table 1 shows the determined maximum fenceline concentrations while one of the wells were being drilled in a landfill cell, in a four day period, at the Lapari landfill site. The measurement configuration was shown in Figure 2a. The concentrations of the listed chemicals were below the detection limits of the FTIR-RS during this activity. By a careful measurement of the MDLs, an upper limit of the path averaged concentrations are determined, resulting in an upper limit on the emission rates. The plume dispersion model was then used to determine the concentrations at the fenceline, downwind of the

drilling activity. The MDL's, which are affected by changes in the humidity and other atmospheric and measurement conditions, vary from one measurement to the next. The second column shows the range of MDL's, measured during the four day period represented in Table 1.

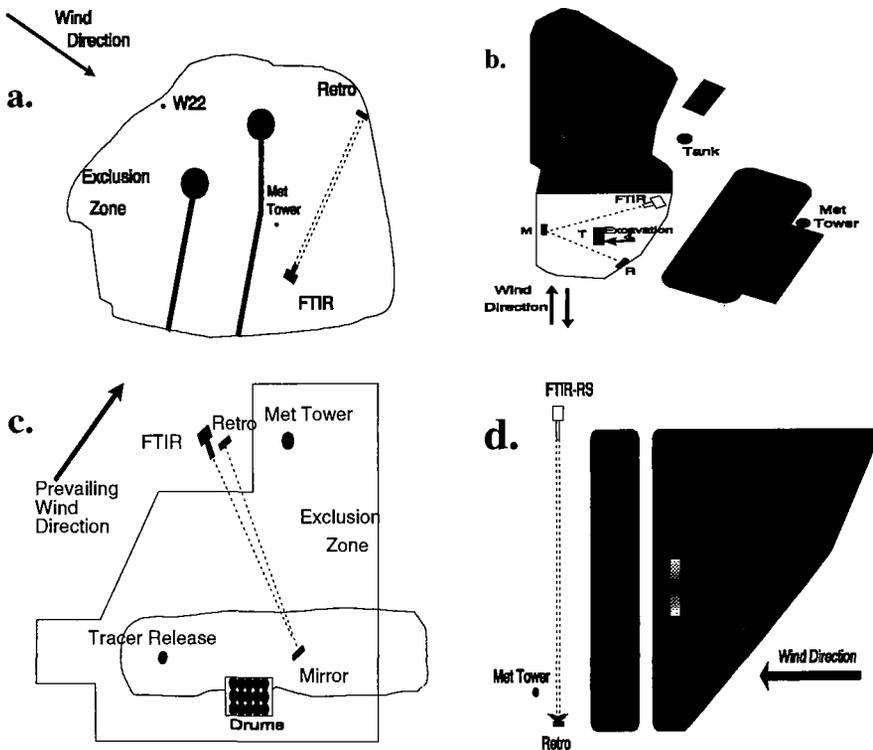


Figure 2 Field Measurement Configurations at the Contaminated Sites.

- a) Lapari Landfill Superfund Site. The FTIR beam path was downwind of drilling activity at well #22. The tracer gas was released at the well.
- b) Gulf Coast Vacuum Superfund Site. A v-shaped beam path configuration was used here because of the frequent 180° change in wind direction. A flat mirror (M) reflected the beam to the retroreflector array at location R. The tracer was released at the location T.
- c) Westminster Superfund Site. A folded beam path was used to double the sensitivity of the measurement. Excavation occurred during this measurement at the tracer release point.
- d) Surface Impoundment (RCRA) Site. The FTIR beam path was downwind of sludge dredging activity in the surface impoundment.

Table 2 shows measurement results for emission rates obtained, in a 35 minute time period, during excavation at the site shown in Figure 2b. The three major components measured here are methane, n-octane, and iso-octane. There was also present higher chain alkanes but because their spectra are similar to octane's, the n-octane concentration was used to represent C8 and higher straight chain alkanes and iso-octane was used to represent C8 and higher branched chains alkanes. The concentrations of all three component were above the detection; thus, these are determinations of actual emission rates.

Table 3 shows maximum emission rates determined at the surface impoundment / RCRA program. The concentrations of the compounds listed here were below the MDL's, so these are upper-limit values. Determined emission rates for sulfur dioxide at the Westminster Superfund site are shown along with a description of the concurrent test remediation activity

are shown in Table 4. The sulfur dioxide concentrations were above the detection limits, thus the emission rates were directly measured.

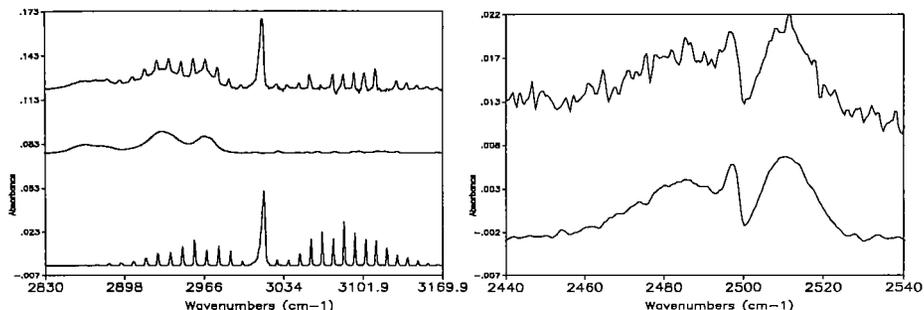


Figure 3 Comparisons of Field Spectra to Laboratory Measured Reference Spectra.

- a) A field spectrum of n-octane and methane, measured at the Gulf Coast Superfund Site, is shown in the upper trace. The middle trace is the reference spectrum for 500 ppm meter of n-octane and the lower trace is the reference spectrum for methane (81 ppm meter). The total round-trip beam path was 240 meters and the resolution was  $1\text{ cm}^{-1}$ .
- b) A field spectrum of sulfur dioxide (377 ppb), measured at the Westminster Superfund Site is shown in the upper trace. The bottom trace is the reference spectrum for sulfur dioxide (476 ppm meter). The total round-trip beam path was 128 meters and the resolution was  $1\text{ cm}^{-1}$ .

## DISCUSSION

The measurement data from these four programs are voluminous. The results shown here are small examples taken from each of the programs, to provide an overview of emergency response applications of FTIR-RS measurements. The FTIR-RS system provides a real time concentration report which includes a goodness of fit number (GOF) which is equal to three times the standard deviation of the classical least-squares fit, propagated to the concentration determination. This number gives a measure of the precision in the concentration determination. It is also used to determine if the CLS result for the concentration is real or a false positive. If the concentration determination is greater than three times the GOF, the CLS calculated value is a measure of the concentration of the absorbing chemical. If the concentration determination is less than three times the GOF, then the concentration of the absorbing chemical is considered to be below the detection limit. If the chemical is known to be present then two times the GOF is used to determine that the CLS determination is not a false positive. The minimum detection limit (MDL), which can vary from one measurement to the next (due to changes in the humidity and other factors), is considered to be equal to two to three times the GOF value. The MDL determination is very important when the concentrations are below the detection limit because it provides an upper limit to the concentration values and an upper limit to the emission rates, two very important determinations.

The precision in the concentration measurements at the four sites ranged around three percent. The accuracy of the concentration measurements are determined by a measurement quality assurance procedure. This involves flowing a reference gas mixture (in which the component concentrations are known to 1 percent accuracy) through a 15 cm spectroscopic gas cell which is situated in the infrared beam path inside of the FTIR sensor. The infrared radiation then passes through both the cell and the atmosphere. The concentration determinations should increase by the concentration of the components in the cell. The deviation from the expected increase is reported as the accuracy. The accuracy of the concentration determinations at the four sites ranged from 3 percent to 33 percent, and for most measurements was around 16 percent. The two most major sources of systematic error in the FTIR-RS concentration determinations are error in the reported concentration-pathlength product for the reference spectrum and baseline errors. The accuracy determinations in the field programs provide us with feedback to help us improve the accuracy of the reference measurements.

The error in the emission determinations predominantly come from inaccurate assumptions in the plume dispersion model, particularly in respect to the vertical dispersion distribution. The ratio technique using Eq (5) gets around this problem nicely, so that the error in the emission rate is propagated from error in the concentration of the absorbing gas, the concentration of the tracer gas, the emission rate of the tracer gas, and error due to imperfect co-location of the tracer emission source to the absorbing gas emission source.

**Table 1** Daily Worst-case Maximum Exposure at the Fenceline of the Lapari Landfill Superfund Site. These determinations were made from measurements at which the concentrations were below the detection limits of the FTIR-RS which in turn were verified by QA procedures. The full range of MDL values over the four day period are given in the second column..

Contaminant	MDL's (mg / m2)	Max. Fenceline Concentration (mg/m3)			
		9/27	9/30	10/1	10/2
Benzene	28 - 120	1.8	1.5	1.2	0.74
Bis(2-chloroethyl) ether	26 - 98	1.5	1.8	0.82	0.77
Toluene	18 - 58	0.87	1.1	0.64	0.46
Xylenes	25 - 59	0.88	1.3	0.81	0.69
Ethyl Benzene	17 - 120	1.9	1.8	0.54	0.47
1,1,1-Trichloroethane	7 - 30	0.45	0.37	0.28	0.18
1,1-Dichloroethane	12 - 52	0.78	0.64	0.49	0.32
1,2-Dichloroethane	74 - 290	4.3	6.3	2.4	2.8
Methylene Chloride	37 - 106	1.6	2.7	1.2	1.4
Chloroform	5 - 13	0.19	0.28	0.19	0.16
Carbon Tetrachloride	4 - 9	0.13	0.20	0.12	0.09

**Table 2** Actual Measured Emission Rates Determine at Gulf Coast Superfund Site.

Time	n-Octane & n-C9+	iso-Octane & iso-C9+	Methane
	g / sec	g / sec	g / sec
15:55	0.034	--	0.38
15:56	0.054	--	0.28
16:01	0.29	0.051	0.30
16:06	0.55	0.10	0.67
16:10	0.43	0.072	0.44
16:12	0.37	0.057	0.54
16:13	0.58	0.096	0.64
16:14	0.51	0.071	0.89
16:18	0.32	0.053	0.21
16:23	0.65	0.11	0.38
16:28	0.91	0.20	0.57

**Table 3** Maximum Emission Rates Determined for Three FTIR-RS Events in the surface impoundment (RCRA) program. The minimum detectable limits (MDL) for FTIR-RS measurements are given in the column labeled MDL.

Compound	MDL	Event B6	Event B14	Event B17
	mg/m2	g / sec	g / sec	g / sec
Benzene	105	2.3	1.2	3.0
Chloroform	8.3	0.21	0.11	0.28
1122- Tetrachloroethane	43.9	0.90	0.48	1.2
Tetrachloroethylene	18.3	0.45	0.23	0.58
Vinyl Chloride	28.1	0.62	0.32	0.80

**Table 4** Actual Sulfur Dioxide Emission Rates Determined from FTIR-RS Measurements at the Westminster Superfund Site for measurement day 5. On this day, two different trenches were dug in an area with subsurface toxic waste.

Meas. Time	SO2	Activity in Trenches
Start	End	g/sec
13:30	13:35	0.55
13:45	13:50	0.92
14:05	14:10	0.45
14:20	14:25	0.73
14:25	14:30	0.54
14:30	14:35	1.1
16:05	16:10	0.07
16:20	6:25	1.0
16:35	6:40	0.42
16:50	16:55	0.41

## CONCLUSIONS

The FTIR remote sensor has shown to be a valuable real-time measurement tool for emergency response to fugitive emissions of toxic air pollutants during remediation of contaminated sites. The use of the FTIR-RS with plume dispersion models allow calculation of the downwind impact of accidental and routine releases, to determine whether human exposure to toxic levels have occurred.

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# A New Concept for Open Path Air Pollution Monitoring

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## ABSTRACT

This monitor concept combines an acousto-optic tunable filter for emission spectroscopy (3.5-14.0  $\mu\text{m}$ ) with a mid-IR (4.6-5.4  $\mu\text{m}$ ) and far-IR laser (9.2-10.9  $\mu\text{m}$ ) for absorption spectroscopy in an instrument for the optical remote measurement of ppb-ppm concentrations of air pollutants. It utilizes commercially available components, is fast (~2 minutes for 120 gases), covers a large area (~6 km path lengths), measures the distance to any reflecting object, and can take measurements along any line-of-sight.

## INTRODUCTION

Concern with atmospheric measurements has grown immensely in recent years with the realization that the quality of human life is significantly impacted by the quality of the air. Over 40 toxic gases<sup>1</sup> and 172 specific Hazardous Air Pollutants<sup>2</sup> (HAPs) are of primary concern. To assure a healthy environment for human life, it is necessary to monitor over large areas the concentrations of these pollutants, most of which are hydrocarbons which have line spectra in the infrared "fingerprint region" of 8-12  $\mu\text{m}$ .

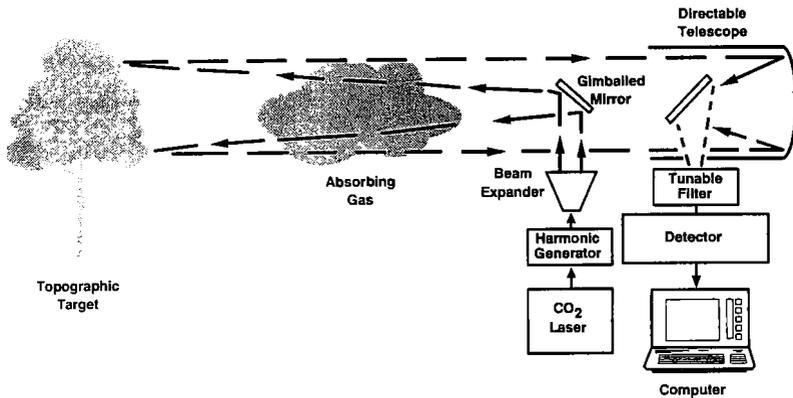
For long open-path remote sensing and quantitative measurements of atmospheric concentrations of trace vapors, differential-absorption lidar (DIAL) is the best technique. Furthermore, infrared DIAL systems are preferred because they are highly sensitive to the laser energy, are relatively "eye safe", and, most importantly, are in the spectral range where most molecular-specific absorption lines occur.<sup>3</sup> Of the available infrared lasers, CO<sub>2</sub> lasers are the best suited for long-path atmospheric monitoring because they have the highest efficiencies and powers, are easily tuned, and cover the 9.2-10.9  $\mu\text{m}$  range which is very rich in molecular-specific spectra. Furthermore, their wavelengths can be extended by harmonic generation to cover the 4.6-5.4  $\mu\text{m}$  range.<sup>4</sup>

However, all laser systems have limited wavelength coverage. Thus, a DIAL system should be complemented with a broader wavelength system. An Acousto-Optic Tunable Filter (AOTF) is a good choice for the complementary system because it is easily integrated into a DIAL system, it monitors emission spectra passively, it can be quickly tuned to any desired wavelength, its sensitivity is easily increased by measuring derivatives of spectra lines, and it covers two wavelength octaves, e.g., 3.5-14.0  $\mu\text{m}$ .<sup>5</sup>

## POLLUTION MONITOR CONCEPT

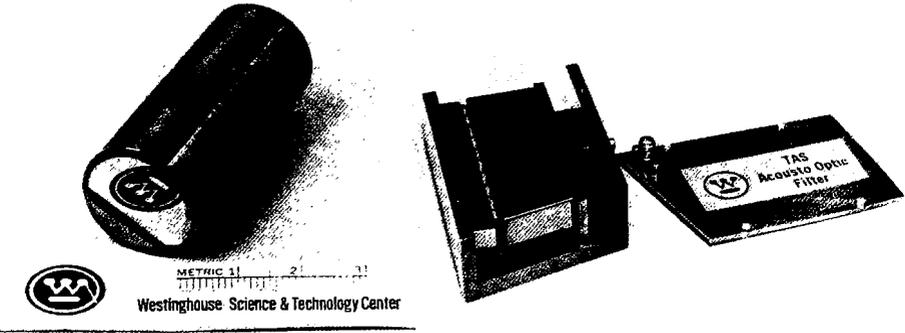
### System Description

The remote monitor, as shown in Figure 1, is comprised of six key elements: a CO<sub>2</sub> laser, a nonlinear crystal, optics, an AOTF, detectors, and a computer. The CO<sub>2</sub> laser is tunable over 87 lines in the 9.2-10.9  $\mu\text{m}$  region where a large multitude of hydrocarbons have absorption spectra. The laser operates at 10 pulses/sec with 1 to 250 mJ/pulse, depending on the line. The pulse width of the linearly polarized beam is 100 nsec.



**Figure 1 – Basic configuration of remote monitor has six key components.**

The CO<sub>2</sub> laser frequency is doubled with a nonlinear crystal, Tl<sub>3</sub>AsSe<sub>3</sub> (TAS). TAS harmonic generators, see Figure 2, are completely passive and have produced the highest measured efficiency in the far infrared, 57%. This crystal will produce pulse energies from 1 to 15 mJ on 68 lines in the 4.6-5.4 μm region. The transmitter optics then enlarges the laser beam to a 20 cm diameter to make it eye safe.

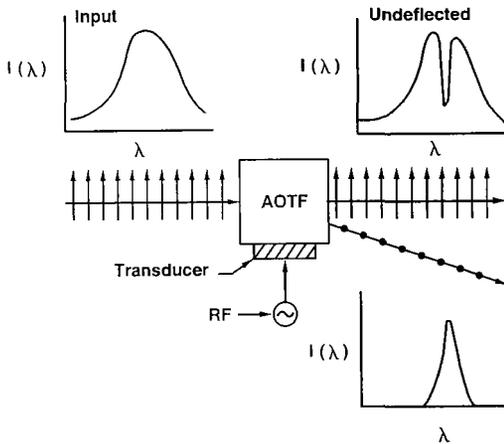


**Figure 2 – Harmonic generator and AOTF are small solid-state components.**

The receiver optics collects the reflected beam with a 30 cm mirror and focuses it through the AOTF onto the detectors. The AOTF is fabricated from a TAS crystal, as shown in Figure 2, and operates as described in Figure 3. The received beam, linearly polarized as indicated by the arrows, enters the crystal and interacts with a periodically varying spatial distribution of indices of refraction set up by an acoustic beam inserted via

the transducer. Only a narrow spectral band,  $\sim 10 \text{ cm}^{-1}$ , will be phase matched to the acoustic beam and diffracted out of the main beam, with its plane of polarization rotated  $90^\circ$  since TAS is a birefringent crystal.

Two detectors are used for improved sensitivity. One detector operates from 7 to 14  $\mu\text{m}$  and one operates from 3.5 to 7  $\mu\text{m}$ . The AOTF directs the received radiation to the two detectors by using one transducer for the 7 to 14  $\mu\text{m}$  portion and a second transducer for the 3.5 to 7  $\mu\text{m}$  portion. The transducers are placed on orthogonal faces of the crystal and diffract the two portions of the beam into two different directions. The detector signals are then analyzed by the computer.



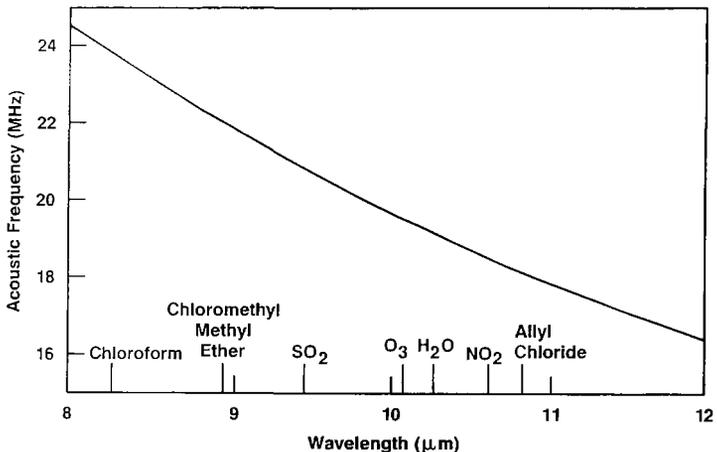
**Figure 3 – AOTFs are electronically-tunable and have narrow pass bands.**

### System Operation

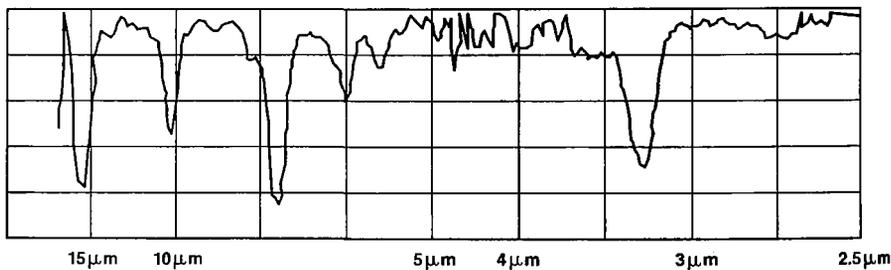
The  $\text{CO}_2$  laser wavelengths are switched in a predetermined pattern, typically staying on each wavelength for one second. Electronically activated two-position mirrors direct the  $\text{CO}_2$  laser beam through the harmonic generator crystal for short wavelength operation and around the crystal for long wavelength operation. An electronically controlled gimbaled telescope directs the beam to any target in real time. Thus, large areas can be quickly monitored via several beam paths and the beam paths quickly changed to respond to fugitive releases wherever they may occur.

The AOTF has two functions. During absorption measurements the AOTF increases the signal-to-noise ratio by restricting radiation from the atmosphere to a narrow spectral range,  $\sim 10 \text{ cm}^{-1}$ , around the absorption line. During emission measurements, the AOTF is operated from 3.5 to 14.0  $\mu\text{m}$ . By careful selection of the acoustic frequency, the wavelength of the diffracted beam can be centered on key emission lines of specific gases, such as shown in Figure 4. These key emission lines can be monitored when absorption

measurements are not being taken, and if preset thresholds are exceeded the laser can be activated for detailed measurements. Alternatively, the entire wavelength region can be scanned to obtain spectra such as the one for benzene shown in Figure 5.



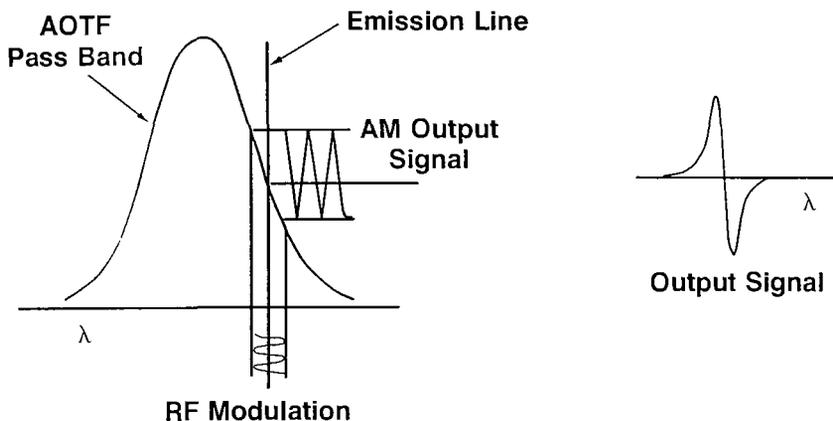
**Figure 4 – AOTF wavelength is centered on a line with the acoustic frequency.**



**Figure 5 – An AOTF-generated benzene spectrum.**

The detectability of sharp emission lines is enhanced by modulating the acoustic frequency at a fixed frequency, ~1 kHz, as shown in Figure 6. This modulation sinusoidally shifts the AOTF passband. The modulation does not affect the radiation from sources which have relatively constant intensities over the AOTF passband, but modulates the intensity from emission lines narrower than the AOTF passband. A lock-in amplifier tuned to the modulation frequency gives the first derivative of the spectra within the AOTF passband. The second derivative is obtained in a similar manner.<sup>5</sup>

The computer determines concentrations and, with a 10 nsec rise time detector, determines the range to the reflecting target to within 2 m. It then stores and displays the results. With associated electronics it also controls the operation of the monitor.



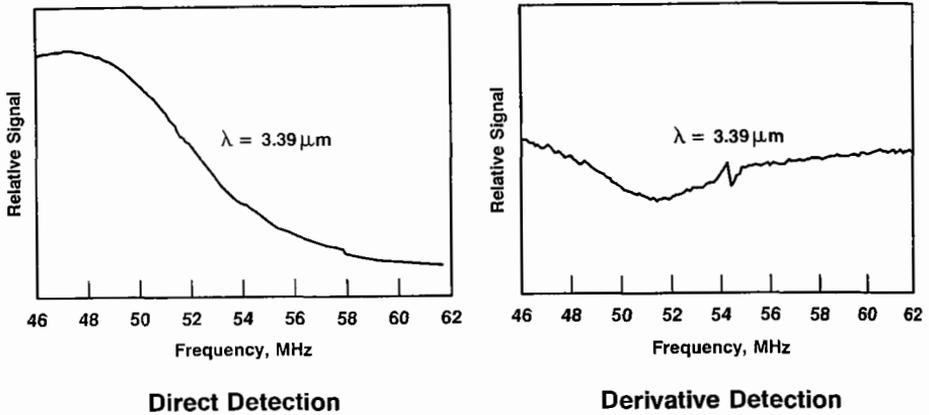
**Figure 6 – AOTF derivative detection is sensitive to narrow-line emissions.**

### System Performance

The laser power is sufficiently large that signal-to-noise over 6 km path lengths is not a problem. In this mode of operation the monitor is essentially the same as other CO<sub>2</sub> DIAL systems and has the same sensitivities. In the 9.2-10.9 μm region, the monitor has the potential to measure concentrations of 101 HAPs and over 40 other vapors of interest. Detection limits vary from 1 ppb for Freon 12 to 60 ppb for ethyl-mercaptan to 340 ppb for sulphur dioxide. In the 4.6-5.4 μm region, the monitor has the potential to measure 16 HAPs and over 14 other vapors of interest. Detection limits vary from 0.3 ppb for carbonyl sulfide to 21 ppb for nitrous oxide to 187 ppb for carbon monoxide.

In measuring emission spectra the large wavelength coverage allows the monitoring of literally hundreds of gases. However, the sensitivity is lower because the emitting gas is at or near the same temperature as the atmosphere which is emitting as a blackbody. Fortunately, atmospheric vapors have narrow line widths which allows the modulation of the AOTF to increase the sensitivity by obtaining first and second derivatives of the spectra. This enhancement is shown in Figure 7 for a laser line with 1% of the spectral radiance of a glow bar in the background. The laser line cannot be seen in direct detection but when the first derivative is taken the laser line is clearly seen.

The concentration sensitivity of this technique can be in the ppb range but is wavelength dependent because of the atmospheric blackbody wavelength dependence. The signal (emission line) to background (atmospheric radiation) ratio is increased, by taking the first derivative, by 9 at 10.6 μm, by 36 at 5.3 μm, and by 75 at 3.7 μm. The second derivative gives enhancements of 68 at 10.6 μm, 1100 at 5.3 μm, and 4700 at 3.7 μm.<sup>5</sup>



**Figure 7**—Measurements of HeNe laser line with 1% the radiance of a glow bar.

## CONCLUSIONS

The extension of the CO<sub>2</sub> laser DIAL system into the 4.6-5.4 μm region increases the coverage of some key gases which do not absorb in the 9.2-10.9 μm region. Designing the DIAL system with a pulsed CO<sub>2</sub> laser and a gimbaled telescope allows the range to any reflecting target to be measured and the monitoring volume to be selected in real time — major operating conveniences. Absorption spectroscopy over a 6 km path length can detect concentrations of over 150 gases to levels of 1 ppb to 340 ppb.

The AOTF in the receiver improves the signal-to-noise ratio in the absorption measurements but its primary advantage is in the 3.5-14 μm emission spectroscopy. Hundreds of gases can be measured in concentration levels down to ppb. These measurements are possible because of the large enhancements in signal-to-background ratios obtained by taking spectral derivatives — an easy task with an AOTF.

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***Session 16***

***Measurement of VOCs***

## **Recovery After Storage and Desorption Efficiencies for Volatile Organic Compounds Spiked on Thermal Desorption Tubes**

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### **ABSTRACT**

Two very important considerations when analyzing samples collected on thermal desorption tubes are 1) the conditions under which the tube must be stored prior to analysis, to assure confidence in the final results, and 2) desorption efficiency of the collected analytes from the tube.

1) Recoveries were determined for 12 halogenated hydrocarbons desorbed from spiked thermal desorption tubes after storage at ambient, refrigerated, and frozen temperatures for 3, 7, and 14 days. We found that three day storage at ambient temperature gave 95% or better recovery of the analytes. Samples stored for the longer time periods also gave acceptable results, when stored at reduced temperatures.

2) Thermal desorption efficiencies were measured after spiking adsorbent tubes with 20 halogenated and nonhalogenated hydrocarbons, in volumes simulating 1.0, 2.0, 3.0, 4.0, and 5.0 air liter samples. Recovery values indicate that, with increasing sample volume, desorption efficiencies decrease for some compounds when the calculations are based on standards prepared using the flash vaporization spiking technique and a 0.5L sample volume.

## INTRODUCTION

The collection of air samples on adsorbent(s) contained in thermal desorption tubes is specified in many USEPA analytical methods [1-3] for the determination of volatile organic compound (VOC) contamination. One important concern about this type of air sampling is the integrity of the sample from the time it is sealed after sampling to the time it is thermally desorbed in the laboratory, to determine VOC concentrations. In our first study, we spiked Carbotrap 300™ multibed thermal desorption tubes, which contain three types of carbon-based adsorbents [4-7], with twelve common halogenated hydrocarbons listed in USEPA methods. The tubes were stored at three temperatures: ambient, refrigerated, and frozen, for three time periods: 3, 7, and 14 days. For each time and temperature combination, recovery of the analytes after desorption was compared to recovery from tubes spiked in an identical manner on the day of analysis.

In a second experiment, we spiked thermal desorption tubes with the same twelve compounds in a similar manner and allowed 1.0, 2.0, 3.0, 4.0, and 5.0L of inert nitrogen to pass through each tube before desorbing the analytes to the gas chromatograph. Recovery values were determined by comparing analyte peak areas for the 1.0-5.0L samples to areas for 0.5L samples. Recoveries for eight nonhalogenated compounds were determined at the 5.0L sample volume.

## EXPERIMENTAL

### Equipment and Materials

A Hewlett-Packard 5890A gas chromatograph (Hewlett Packard, Avondale, PA) equipped with an electrolytic conductivity detector (OI Analytical, College Station, TX), a Dynatherm Model 890 thermal desorption unit (TDU), Carbotrap 300 thermal desorption tubes (11.5cm x 6mm OD x 4mm ID glass) containing 300mg 20/40 mesh Carbotrap C, 200mg 20/40 mesh Carbotrap B and 125mg 60/80 mesh Carbosieve™ S-III, and a VOCOL™ capillary column (105m x 0.53mm ID x 3.0µm phase film) (all from Supelco, Inc., Bellefonte, PA) were used in this work. Analytical standard mixtures were also supplied by Supelco.

### Tube Spiking

Three common tube spiking techniques are cited in EPA methods for calibration in thermal desorption techniques: permeation device(s), static dilution, and flash vaporization [1,2]. In both studies we employed the flash vaporization technique, utilizing the injection port and secondary trapping port of the thermal desorption system (Figure 1). Injections of the analyte mix, 20ng each compound in 0.2µl of methanol, were made by syringe through this injection port, into an empty tube in the desorption chamber, heated to 200°C. Inert nitrogen (50ml/min) swept the volatilized analytes from the desorption chamber to a Carbotrap 300 tube in the secondary trapping port at the end of this heated pathway. The tube was retained in the secondary trapping port for the time necessary to achieve the desired sample volume.

### Thermal Desorption

Carbotrap 300 tubes containing the adsorbed analytes were desorbed to the gas chromatograph at 330°C for 5 minutes with approximately 8ml/min carrier gas, with the flow directed to the capillary column. The long length (105m) and thick film (3.0µm) eliminated the need for a secondary refocusing device or the use of cryogenics to focus the analytes. An ELCD detector was used to detect the halogenated compounds because it has high sensitivity for these compounds and does not respond to methanol. A flame ionization detector (FID) was used to detect the nonhalogenated compounds.

### Tube Storage Study

For each storage time interval, nine identical tubes were spiked with 20ng of each analyte. Each tube was removed from the secondary trapping port after exactly 10 minutes, giving a sample volume of 0.5L. Upon removal from the secondary trapping port, the tubes were sealed in glass storage containers. Three tubes were placed in each of three paint cans containing a small amount of activated charcoal to minimize the chance of outside contamination. One can was left

on the laboratory bench, one can was placed in a refrigerator, and one was placed in a freezer. The average temperature readings over the storage study were 25°C, 4°C, and -27°C, respectively. After 3 days storage, three tubes were removed from each paint can and were allowed to equilibrate to room temperature before desorption. Three standard calibration analyses were conducted intermittently within the nine sample set (12 tubes total). The peak area responses were normalized to an internal standard and averaged within each temperature study (e.g., mean of three normalized area counts for the refrigerated tubes, etc.) and for the calibration analyses. Percent recovery was then determined, using the mean value for the calibration analyses as 100%. This procedure was then repeated for the 7 and 14 day storage time periods. The calculated values of recovery for the analytes are listed in Table 1.

#### Desorption Efficiency Study

The tube spiking technique described above was also used in this study. A mix containing 40ng of each analyte in 0.2µl of methanol was flash vaporized into a 50/ml/min nitrogen flow and directed to the Carbotrap 300 adsorbent tube. The tube was retained under the flow conditions for the time necessary to achieve the desired sample volume. Three analyses each were made for sample volumes of 1.0, 2.0, 3.0, 4.0, and 5.0L. An internal standard was used to normalize area counts before the three analyses for each sample volume were averaged. Desorption efficiencies were calculated by using the mean for three 0.5L analyses as a 100% value. Separate means for 0.5L analyses were determined for each sample volume study. Data showing these percent recoveries are listed in Table 2. A 5.0L analysis was done with eight nonhalogenated compounds; results are listed in Table 3.

#### DISCUSSION / CONCLUSIONS

Data obtained in the temperature - storage time investigation revealed that, ideally, adsorbent tubes containing airborne volatile organic compounds should be stored at reduced temperatures until analysis. A high confidence in sample integrity could be realized, for the analytes studied, when the analytes were stored on 11.5cm x 4mm ID Carbotrap 300 tubes at ambient temperature for three days. However, after three days, the tubes must be stored at reduced temperatures, preferably frozen.

Data obtained in the desorption efficiency study showed that as the sample volume increases, the amount of a specific analyte desorbed from the tube may become increasingly less than the amount collected, when compared to calibration standards prepared using a lower total sample volume.

Analyte desorption efficiency for any sample may decrease with increasing sample volume, since the analyte could migrate through the adsorbent bed that has the most affiliation for it and enter a stronger adsorbent which may not release it as efficiently. Breakdown of heat-sensitive analytes also is more likely with increasing sample volume, because longer retention of the analyte on the adsorbent is expected as a result of further migration/stronger adsorption within the adsorbent beds. This increased retention will prolong the analyte's exposure to the heat required for desorption.

#### RECOMMENDATIONS

In neither study were the effects of humidity investigated. Humidity effects are being considered for future work. Alternative storage devices which reduce the amount of dead volume for analyte migration also are being investigated at this time. This becomes more important for smaller adsorbent tubes containing less adsorbent material.

The use of permeation devices to spike thermal desorption tubes with constant concentration over the entire sample volume will be investigated, and results will be compared to these values obtained by using the flash vaporization method.

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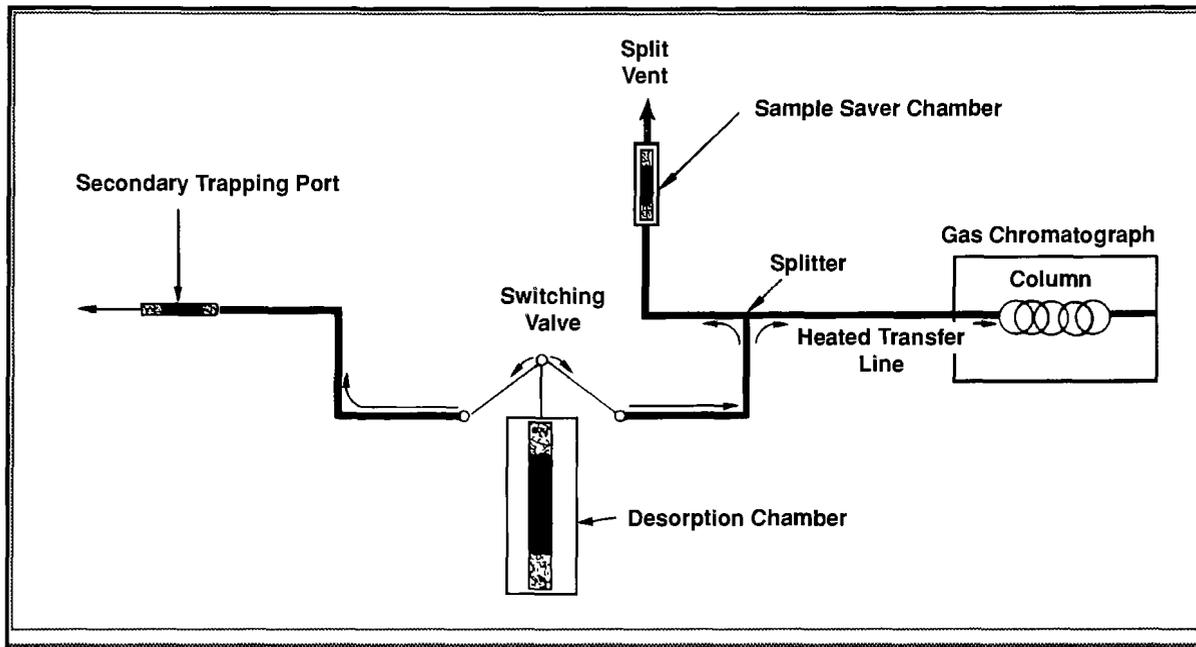


Figure 1. Flow pathways in the thermal desorption unit

Table 1. Mean percent recovery ( $\pm$  standard deviation) of chlorinated hydrocarbons stored on Carbotrap 300 thermal desorption tubes.

Analyte	3 Days			7 Days			14 Days		
	Ambient	Refrigerated	Frozen	Ambient	Refrigerated	Frozen	Ambient	Refrigerated	Frozen
Chloroform	95.7 $\pm$ 1.5	103.8 $\pm$ 0.7	102.2 $\pm$ 1.0	79.5 $\pm$ 10.2	99.1 $\pm$ 2.1	103.3 $\pm$ 1.6	73.8 $\pm$ 11.8	104.3 $\pm$ 1.4	109.8 $\pm$ 3.3
1,1,1-Trichloroethane	100.9 $\pm$ 3.2	104.9 $\pm$ 0.5	103.2 $\pm$ 0.7	94.3 $\pm$ 2.1	96.8 $\pm$ 2.2	98.8 $\pm$ 0.6	96.0 $\pm$ 2.5	102.5 $\pm$ 1.7	102.2 $\pm$ 5.5
Carbon tetrachloride	102.9 $\pm$ 2.8	105.8 $\pm$ 0.4	105.8 $\pm$ 1.4	98.9 $\pm$ 1.1	99.7 $\pm$ 1.1	103.1 $\pm$ 1.4	99.7 $\pm$ 3.7	103.7 $\pm$ 0.7	105.6 $\pm$ 4.0
1,2-Dichloroethane	97.7 $\pm$ 1.5	101.4 $\pm$ 0.8	102.2 $\pm$ 2.8	87.3 $\pm$ 5.4	98.7 $\pm$ 1.6	103.5 $\pm$ 2.3	78.0 $\pm$ 17.6	98.9 $\pm$ 1.2	104.2 $\pm$ 3.0
Trichloroethylene	104.0 $\pm$ 1.6	102.5 $\pm$ 0.9	103.3 $\pm$ 1.3	103.3 $\pm$ 0.4	99.7 $\pm$ 1.8	102.5 $\pm$ 1.1	105.0 $\pm$ 1.7	103.4 $\pm$ 0.6	103.0 $\pm$ 1.8
1,2-Dichloropropane	101.5 $\pm$ 3.2	103.4 $\pm$ 0.7	102.7 $\pm$ 0.4	100.2 $\pm$ 3.0	100.8 $\pm$ 2.2	100.4 $\pm$ 1.2	101.3 $\pm$ 1.8	104.0 $\pm$ 0.6	100.1 $\pm$ 4.2
1,3-Dichloropropane	102.1 $\pm$ 1.8	102.1 $\pm$ 0.2	100.6 $\pm$ 1.1	97.9 $\pm$ 1.9	96.6 $\pm$ 1.8	100.1 $\pm$ 1.4	100.5 $\pm$ 1.3	102.3 $\pm$ 1.4	100.9 $\pm$ 2.0
Tetrachloroethylene	102.1 $\pm$ 1.8	102.1 $\pm$ 0.2	100.6 $\pm$ 1.1	97.9 $\pm$ 1.9	96.6 $\pm$ 1.8	100.1 $\pm$ 1.4	100.5 $\pm$ 1.3	102.3 $\pm$ 1.4	100.9 $\pm$ 2.0
Ethylene dibromide	108.9 $\pm$ 4.9	106.2 $\pm$ 3.8	94.1 $\pm$ 7.8	95.3 $\pm$ 1.9	100.2 $\pm$ 5.4	91.8 $\pm$ 5.8	99.6 $\pm$ 3.6	107.5 $\pm$ 3.2	108.7 $\pm$ 7.2
Chlorobenzene	102.1 $\pm$ 1.4	99.6 $\pm$ 1.6	99.6 $\pm$ 0.5	99.0 $\pm$ 0.7	97.1 $\pm$ 3.0	99.4 $\pm$ 1.9	102.9 $\pm$ 1.0	103.3 $\pm$ 1.1	102.1 $\pm$ 1.3
Bromoform	102.2 $\pm$ 4.4	104.3 $\pm$ 1.9	104.1 $\pm$ 3.6	93.6 $\pm$ 4.4	99.5 $\pm$ 5.5	95.2 $\pm$ 2.2	98.1 $\pm$ 2.7	111.1 $\pm$ 2.3	106.2 $\pm$ 5.7
Bromobenzene	104.0 $\pm$ 0.8	100.8 $\pm$ 3.6	101.7 $\pm$ 2.5	98.0 $\pm$ 1.8	97.5 $\pm$ 3.7	95.5 $\pm$ 2.2	107.8 $\pm$ 8.5	105.7 $\pm$ 2.7	102.6 $\pm$ 1.6

Table 2. Mean percent recovery ( $\pm$  standard deviation)\* of chlorinated hydrocarbons from Carbotrap 300 thermal desorption tubes challenged by sample volumes of 1-5L.

Analyte	Sample Volume				
	1 Liter	2 Liters	3 Liters	4 Liters	5 Liters
Chloroform	103.4 $\pm$ 3.9	99.1 $\pm$ 3.3	94.3 $\pm$ 2.1	85.4 $\pm$ 8.5	70.4 $\pm$ 19.1
1,1,1-Trichloroethane	100.2 $\pm$ 4.4	94.2 $\pm$ 3.8	88.5 $\pm$ 3.9	84.8 $\pm$ 2.7	82.8 $\pm$ 3.0
Carbon tetrachloride	100.7 $\pm$ 5.9	98.7 $\pm$ 3.4	94.3 $\pm$ 3.7	92.3 $\pm$ 2.1	90.6 $\pm$ 3.9
1,2-Dichloroethane	102.5 $\pm$ 3.6	102.5 $\pm$ 2.5	99.6 $\pm$ 2.5	101.1 $\pm$ 1.6	103.2 $\pm$ 1.2
Trichloroethylene	102.1 $\pm$ 2.9	103.0 $\pm$ 2.6	99.3 $\pm$ 1.9	101.3 $\pm$ 0.5	102.6 $\pm$ 0.3
1,2-Dichloropropane	101.2 $\pm$ 3.1	100.9 $\pm$ 3.4	98.6 $\pm$ 2.7	97.8 $\pm$ 1.2	99.3 $\pm$ 0.9
1,3-Dichloropropane	91.0 $\pm$ 5.7	87.6 $\pm$ 2.9	83.3 $\pm$ 2.4	75.8 $\pm$ 0.2	76.5 $\pm$ 1.5
Tetrachloroethylene	98.6 $\pm$ 4.5	101.2 $\pm$ 3.3	102.1 $\pm$ 2.6	98.1 $\pm$ 0.8	101.4 $\pm$ 0.8
Ethylene dibromide	79.0 $\pm$ 5.4	65.3 $\pm$ 2.6	58.9 $\pm$ 1.8	48.0 $\pm$ 0.2	47.1 $\pm$ 2.5
Chlorobenzene	99.1 $\pm$ 0.8	102.7 $\pm$ 2.7	102.6 $\pm$ 1.8	100.3 $\pm$ 1.3	100.6 $\pm$ 2.0
Bromoform	94.7 $\pm$ 6.9	88.4 $\pm$ 3.7	85.6 $\pm$ 1.1	85.3 $\pm$ 0.6	79.1 $\pm$ 6.8
Bromobenzene	100.5 $\pm$ 1.2	100.1 $\pm$ 1.0	100.2 $\pm$ 1.4	100.5 $\pm$ 0.4	98.6 $\pm$ 3.5

\*Peak areas normalized to internal standard (2-chlorotoluene).

**Table 3. Mean percent recovery of nonhalogenated hydrocarbons from Carbotrap 300 thermal desorption tubes (5L samples).**

<b>Analyte</b>	<b>% Recovery</b>
1-Heptene	99.3
Benzene	100.3
Toluene	100.3
Ethylbenzene	100.4
m-Xylene*	100.5
p-Xylene*	100.5
o-Xylene	99.6
Isopropylbenzene	100.0
*coeluting analytes	

## TEMPORAL AND SPATIAL VARIABILITY OF TOXIC VOC SOURCES IN COLUMBUS, OHIO

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### ABSTRACT

Source apportionment modeling was conducted on a data set of 142 3-hr integrated air samples collected at 6 different sites and in 3 separate campaigns during the summer of 1989 in the U.S. EPA's Columbus (OH) Hazardous Air Pollutants (HAPS) program. Source contributions to 19 light hydrocarbon and toxic VOC species, including formaldehyde and acetaldehyde, were modeled. Overall, the results indicated that the mobile and area source categories, the latter defined as fixed, non-point sources, and specifically, vehicle exhaust and organic solvent usage by small industrial/commercial facilities, were the main contributors to the major toxic VOCs. A number of observations regarding the short-term variability of the sources were also made, including diurnal trends in the vehicle exhaust, and gasoline vapor sources.

### INTRODUCTION

Exposure to hazardous air pollutants (HAPs), including volatile organic compounds (VOCs), is believed to result in significant risks to human health. Recent research has shown that many of the toxic/hazardous VOCs present in urban air, such as benzene, toluene, and xylenes, originate predominantly from mobile (*i.e.*, vehicular) and area source emissions, rather than from industrial point sources.<sup>1-3</sup> These studies have demonstrated, using chemical mass balance (CMB) source apportionment modeling, that even in the vicinity of large industrial point sources such as refineries and chemical plants, significant fractions of the air concentrations of the major VOC species are attributable directly to vehicle exhaust, gasoline vapor, and area source emissions.

The source-receptor studies conducted thus far, however, have not included the time resolution and multiple sampling sites needed to assess the variability in VOC source contributions over short temporal and spatial scales. This information is particularly relevant in urban areas, where time-varying area and mobile source emission patterns can result in spatial variabilities within and between neighborhoods, and in diurnal concentration trends and differences between short-term peak concentrations and long-term means. The modeling conducted in this study attempts to address some of these issues.

### Study Background and Measurements

The source attribution study conducted was a part of the broader Columbus HAPS field study conducted by Battelle<sup>4</sup> for the U.S. EPA in June-July 1989. The broader study addressed a number of issues pertaining to human exposure to HAPs, with a primary focus on the spatial and temporal variability of the HAPs concentrations in urban areas and of the key area sources of these HAPs.

The Columbus, Ohio, metropolitan area selected for the study has a population of over 1 million people, thus assuring a sufficient source strength of area and mobile sources in the region. In addition, the region does not contain any large industrial point sources such as refineries and chemical plants. The absence of major point sources facilitates the study of the area and mobile sources believed to be responsible for most of the HAP concentrations in urban areas.

Six measurement sites for the study were selected within the region, based on meteorology, population density, traffic density, location of residential neighborhoods, and the zones of commercial and industrial activity. The various sites were selected to provide spatial resolution at site-to-site distances from 1 to 10 km, both in the SW-NE and the NW-SE directions (in and perpendicular to the direction of the prevailing winds, respectively). One of six sites (Site 1) was located in closest to the center of the city in a predominantly commercial/business area, and was surrounded by heavily traveled traffic corridors, numerous large parking lots, small area sources such as printing and publishing facilities, gasoline stations, and small industries that use various chemical solvents. The other five sites were located in residential neighborhoods, at differing distances from highways and commercial zones.

A variety of samples were collected and analyzed in the study at each of the six sampling sites.<sup>4</sup> The primary sampling protocol at all six sites was integrated sampling over successive 3-hour intervals using canister sampling for VOCs and dinitrophenylhydrazine (DNPH) impinger sampling for carbonyl compounds. At all sites, sampling was carried out for eight 3-hour periods each day, during three separate 2-day campaigns: June 20-22, June 28-30, and July 11-13, 1989. Each 2-day campaign contained 16 3-hour sampling intervals, for a total of 48 spatial samples at each of the six sites for each of the species measured.

## **SOURCE APPORTIONMENT**

### **Modeling Method**

The Chemical Mass Balance (CMB) modeling approach, involving multiple linear least-squares regression analysis, was employed in this study for apportioning the sources of the various VOC species selected from the complete list of VOC species measured in the field study. The application of CMB modeling to VOC source apportionment has been discussed previously<sup>5,6,7,1,2</sup>.

A total of 19 VOC species were selected for inclusion in this modeling study, from the complete list of VOC species measured at the six sites.<sup>4</sup> The list comprised 14 hydrocarbons (ethane, propane, i-butane, n-butane, i-pentane, n-pentane, acetylene, ethylene, propylene, benzene, toluene, o-xylene, m+p-xylene, ethylbenzene), 3 chlorinated hydrocarbons (1,1,1-trichloroethylene, perchloroethylene, and dichloromethane), and 2 aldehydes (formaldehyde and acetaldehyde). A few of the VOC species modeled were not used as fitting species; i.e., their inclusion in the model did not influence the source apportionment results. These species included dichloromethane, formaldehyde, and acetaldehyde, which were not fitted because the source profiles contributing to these species were too few or too uncertain, and acetylene and propylene, which were often not fitted because of concerns about the data quality for these species.

All of the fitted VOC species are expected to have lifetimes in the urban atmosphere of at least several hours, and up to a half-day or more in many cases.<sup>5</sup> Since the travel times from the VOC sources to the sampling sites in the study area are likely to be much shorter, on the order of 1 hour or less, the reactivity of the VOC species fitted in the model was not expected to interfere with the CMB modeling analyses conducted in this study.

### **Emissions Inventory**

A review of the National Emissions Data System (NEDS)<sup>6</sup> and the U.S. EPA's Toxic Release Inventory System (TRIS)<sup>7</sup> listings for Franklin County for 1989 confirmed that Columbus did not contain any major point sources of VOCs, but rather, contained numerous minor point sources (or "area" sources) identified in the TRIS listings as emitting various amounts of solvents such as toluene, xylenes, and chlorinated hydrocarbons. A review of the Greater Columbus Industrial Redliner<sup>8</sup> showed that these area sources were generally scattered throughout much of Franklin County.

### **Source Profiles**

The complete spectrum of source profiles previously developed in the literature for VOC sources was assembled, including those from the U.S. EPA's SPECIATE database,<sup>9</sup> papers by Scheff, *et al.*,<sup>1</sup> and Sweet and Vermette,<sup>2</sup> as well as several other references cited in these papers. Profiles representing sources that were not physically present in the Columbus area were first eliminated from consideration. Subsequently, the most appropriate source categories for modeling the Columbus VOC database were identified by using various combinations of source profiles to apportion the measured VOC concentrations. A list of five refined source profiles was thus identified, representing source categories of vehicle exhaust, gasoline vapor, natural gas, industrial solvent usage (toluene, xylenes) and chlorinated solvent usage, the latter believed to be tied to (dry)cleaning, degreasing, and wastewater operations (CDW).<sup>4</sup>

## **RESULTS**

### **Campaign-Average Data - Overview and Spatial Analysis**

Campaign-average data sets were prepared by averaging together the 16 consecutive 3-hr samples from each site in each 2-day sampling campaign, yielding 18 campaign-average data sets (3 campaigns x 6 sites). The source apportionment results for the composited data showed that vehicle exhaust, gasoline vapor, and natural gas were the main sources of each of the modeled VOCs at all six sites, with industrial solvents and the CDW source contributing to specific toxic VOCs. The relative proportions contributed by the various sources were remarkably similar at the six sites, *i.e.*, spatial differences were small, at least when compared

over 2-day averaging periods. This observation confirms that the sources identified are area and mobile sources, in that they affect VOC concentrations comparably at all six of the widespread sampling sites. Temporal differences between the various source contributions also appeared to correlate well with the meteorological conditions in the three campaigns.<sup>4</sup>

The results from the six sites were composited to provide an overview of the ambient concentrations and source contributions in Columbus for each of the major toxic VOC, as shown in Table 1. Table 1 shows that the sum of the source contributions for each species was generally within  $100 \pm 20\%$  of the measured average concentration, indicating adequate source identification. The sums of the source contributions for dichloromethane, formaldehyde and acetaldehyde are low, as expected, since profiles exist for only some of the sources of these compounds; this study is one of the first to include formaldehyde and acetaldehyde in CMB modeling for VOCs. Table 1 indicates that on average, vehicle exhaust contributed about 17% of the measured formaldehyde and 11% of the acetaldehyde. The remaining unexplained portions of these compounds presumably come from photochemical oxidation of atmospheric VOCs, and possibly from other as-yet-uncharacterized, direct emissions sources.

Table 1 emphasizes the importance of vehicle exhaust as a source of the most common toxic aromatic VOCs, namely benzene, toluene and xylenes. Natural gas, an important contributor of the light hydrocarbons, was crucial to achieving good model fits, but contributes very little to toxic VOCs. Gasoline vapor likewise contributes substantially to the light hydrocarbons in Columbus, but is also a minor contributor to the measured toxic VOC concentrations. In contrast, the industrial solvent and CDW sources are minor contributors to light hydrocarbons, but are important contributors to individual toxic VOCs. The industrial solvent source particularly contributes to the aromatic VOCs, excluding benzene; the drycleaning source profile accounts reasonably well for the measured concentration of the chlorinated solvents, and also contributes substantially to benzene and toluene. These results are consistent with those obtained in other CMB source apportionment modeling studies of urban areas in the U.S.<sup>e.g. 1-3</sup>

#### Modeling of 3-Hour VOC Data for Temporal Variability Analysis

The 3-hr VOC data sets collected at Sites 1, 2, and 5 were selected for further CMB source apportionment modeling. The motivation for modeling the 3-hr VOC data sets was the potential for identifying temporal, and spatial phenomena from the enhanced time resolution available in these data.

Figures 1(a,b) show the short-term temporal trends in the relative source contributions to benzene and toluene, for the 16 consecutive 3-hr VOC data sets collected at Site 1 during Campaign 1; similar analyses were conducted for other VOC species, sites and sampling campaigns.<sup>4</sup> The results for benzene (Figure 1a) reveal that vehicle exhaust was the predominant contributor (> 90%) to the measured concentrations. Gasoline vapor and the CDW composite source together contribute typically 5-10% to the measured levels of benzene, and natural gas contributes a trace fraction. No diurnal trends were discerned in the modeled percentage source contributions probably due to the fact that a single source, vehicle exhaust, was responsible for the predominant fraction of measured benzene levels.

Figure 1(b) shows the results for toluene at the same site and campaign. Toluene was attributed primarily to vehicle exhaust, industrial solvent usage, and the CDW composite source, with a trace contribution from gasoline vapor. Again, no significant diurnal trends are discernible, although the industrial solvent contributions to the toluene levels vary sporadically during the campaign. The CDW composite source contributions to toluene are generally stable.

A number of other observations regarding the spatial and temporal variability of the VOC sources were also made from the results of modeling,<sup>4</sup> including the following:

- For both residentially and commercially-located sampling sites, the absolute vehicle exhaust contributions were characterized by a peak between 6-9 a.m., followed by lower levels during the day and a second peak in the late evening hours from 9 p.m.-midnight, and a minimum between 3-6 a.m. These trends are consistent with the traffic activity patterns that characterize urban areas. The occurrence of the second peak during the 9 p.m.-12 a.m. hours rather than during the 6-9 p.m. period corresponding to the evening rush hours may be due to summer-time, evening-hour meteorological conditions that result in poor dispersion of vehicle exhaust emissions.
- On average, the absolute source contributions from gasoline vapor were similar to each other at the residential sites, and lower during the daytime hours than during the corresponding night time hours. At the commercial site, the opposite trend prevailed with daytime absolute gasoline vapor contributions generally higher than the corresponding night time contributions. The contributions between the hours of

midnight-6 a.m. were similar at all sites, but slightly higher at the residential sites. These results suggest that the gasoline vapor source is correlated to a greater extent with the location and presence of parked or moving vehicles, than with fixed locations such as gasoline refueling stations, as previously theorized.

Other observations were also made from model results, such as the variability of vehicle exhaust and gasoline vapor contributions with ambient temperature, and the variability of the natural gas source, industrial solvent, and CDW source contributions.<sup>4</sup>

### VOC Emissions Estimates

The results from this study can also be used to make estimates of the area-wide emissions from various source categories for specific VOCs. Columbus is located in predominantly agricultural central Ohio with no other significant urban areas within a 60 mile radius; the transport of background concentrations of modeled VOCs into Columbus can thus be reasonably assumed to be negligible. A simple box model analysis can then be used to characterize the dilution of VOCs in the Columbus area according to the relation,  $C = Q/(U L M)$ , where C is the VOC species concentration, U is the wind speed, L is the mean cross-sectional dimension of the geographical area, and M is the mixing height. For the 6 sampling days in this study, the average wind speed was ~ 8 km/hr and the average mixing height was ~ 850 m.

Table 2 shows the results of calculations using this approach for the most common toxic VOCs based on the study-average measured concentrations and source apportionment results in Table 1. Table 2 shows that benzene and ethylbenzene are predominantly emitted by mobile sources; toluene releases are similar for mobile and area source; the two chlorinated organics originate only from area sources. Table 2 also shows the fractions of these estimated area source emissions for each species that are represented in the TRIS listings<sup>8</sup> for Franklin County. The small TRIS-reported fractions for all of the species suggest that the majority of the area source emissions for these VOCs probably originate from the numerous smaller facilities that are not included in the TRIS listings; these results are similar to those reported by Sweet and Vermette,<sup>2</sup> using a box model approach for two study areas located in Chicago and East St. Louis, IL.

### CONCLUSIONS

This study addressed the significance and short-term variability of mobile and area source contributions to urban toxic VOCs, measured at several sites in Columbus, Ohio. The study showed that the major sources contributing to the measured VOCs in the region are vehicle exhaust, gasoline vapor, natural gas, industrial solvents, and a composite of cleaning/degreasing/ wastewater activities. The small degree of spatial variability within the region of the relative source contributions to toxic VOCs suggested the ubiquitous nature of these sources. Using the 3-hr integrated samples also allowed evaluation of VOC source variability to an extent not possible with the 24-hr samples normally used in CMB modeling.

The CMB modeled source contributions were combined with a simple box model of the study area to estimate the emission rates of area sources. The results from this analysis suggest that substantial toxic VOC emissions from area sources are likely not included in current emissions inventories.

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Table 1. Summary of CMB model results from campaign-averaged 3-hr data, composited over all six sites and all three campaigns.

Modeled Species	Measured Average Conc. ( $\mu\text{g}/\text{m}^3$ )	Source Contributions (% of measured average concentration)					Sum of Source Contributions (%)
		Vehicle Exhaust	Gasoline Vapor	Natural Gas	Industrial Solvents	CDW <sup>a</sup>	
Light Hydrocarbons <sup>b</sup>	33.4	20	36	45	0	0	101
Benzene	1.5	96	9	2	0	10	117
Toluene	5.1	59	2	0.3	28	26	115
Xylenes	4.9	55	0.2	0	42	1	98
Ethylbenzene	1.1	56	0.7	0	19	0	76
1,1,1-Trichloroethane	4.0	0	0	0	0	89	89
Perchloroethylene	1.6	0	0	0	0	96	96
Dichloromethane	1.5	0	0	0	0	42	42
Formaldehyde	3.8	17	0	0	0	0	17
Acetaldehyde	2.4	11	0	0	0	0	11

<sup>a</sup> CDW: Drycleaning/degreasing/wastewater composite source.

<sup>b</sup> Sum of ethane, propane, butanes and pentanes

Table 2. Comparison of annual toxic VOC emissions calculated using a box model and based on study-average measurements and source apportionment results.

Toxic VOC	Mobile Source Emissions <sup>1</sup> (tons/yr)	Area Source Emissions <sup>2</sup> (tons/yr)
Benzene	2,200	220 (0.4%)
Ethylbenzene	1,400	460 (0.7%)
Toluene	4,500	3,900 (3.1%)
Xylenes	4,500	3,500 (3.4%)
1,1,1-Trichloroethane		6,600 (1.7%)
Perchloroethylene		2,600 (2.0%)

<sup>1</sup> Includes vehicle exhaust and gasoline vapor

<sup>2</sup> Percentage values indicate the fraction of the estimated area source release for each species that is accounted for by the TRIS database

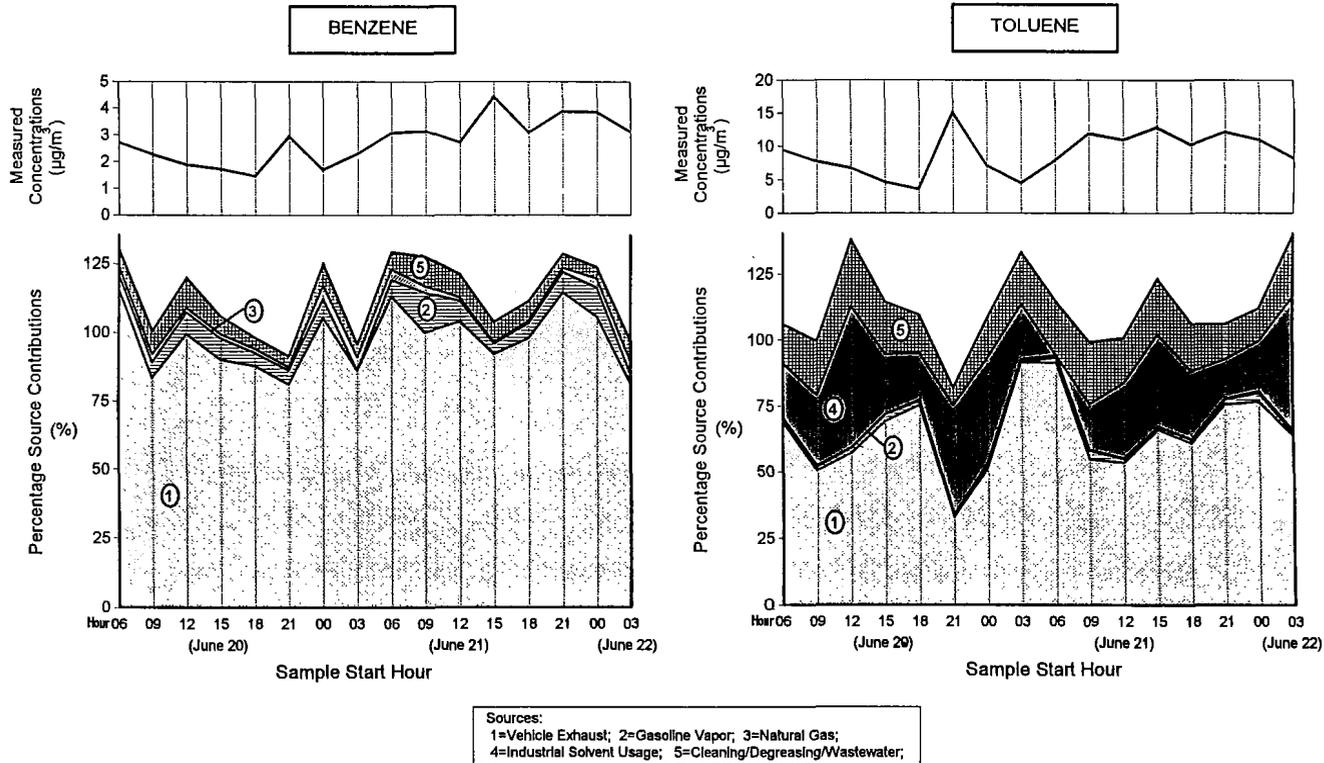


Figure 1. Modeled percentage source contributions (bottom) during sixteen (16) 3-hour intervals at Site 1 (located in a commercial area of Columbus) during Campaign 1 to the measured (shown at top) (a) benzene, and (b) toluene concentrations. Values shown apply to 3-hour intervals in the six sampling days, e.g., "06" applies to the period 0600-0900 hours, etc.

**A Method For Separating Volatile Organic Carbon From 0.1 m<sup>3</sup> Of Air  
To Identify Sources Of Ozone Precursors via Isotope (<sup>14</sup>C) Measurements\***

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**ABSTRACT**

Atmospheric non-methane volatile organic compounds (VOCs) are known to play an important role in urban ozone formation during the summer. To respond to the need for a direct measure of VOC source contributions from biogenic (<sup>14</sup>C/<sup>12</sup>C = 10<sup>-12</sup>) and fossil fuel (<sup>14</sup>C/<sup>12</sup>C = 0) emissions, a system and protocol are being developed to separate the total VOC fraction, which would amount to micrograms of carbon, from 0.1 m<sup>3</sup> of ambient air for accelerator mass spectrometry (AMS) <sup>14</sup>C. The gas separation system developed at NIST allows for the simultaneous separation of *low vapor pressure (LVP) VOCs* and H<sub>2</sub>O, *high vapor pressure (HVP) VOCs* and CO<sub>2</sub>, CO and CH<sub>4</sub> through sequential cryogenic separation and selective oxidation techniques. Preliminary results of this system and procedure for isolating these fractions show a *LVP-VOC* blank of 2 ± 1 μg C, 95% confidence limits, which represents the effect of the separation system plus CO<sub>2</sub> cross-contamination. Hydrocarbons having vapor pressures greater than n-decane are not retained at a level of more than a few percent in the *LVP-VOC* fraction. The yield for *LVP-VOC* fraction is greater than that predicted based strictly on GC/FID analysis of hydrocarbons from the canister given the amount of air processed. Since oxygenated species were not among those compounds reported, but may exist as some of the unidentified compounds, the question remains as to whether or not this class of compounds would have a significant effect on the carbon recovered from the *LVP-VOC* fraction. An upper limit of the *HVP-VOC* blank has been estimated at 7 ± 8 μg C. The recovery of C<sub>5</sub>-C<sub>8</sub> hydrocarbons in the combined *HVP-VOC* and CO<sub>2</sub> fraction ranges from 27% to 78%. Lower recoveries were observed for these same compounds in a hydrocarbon standard having 2 orders of magnitude less CO<sub>2</sub> than ambient concentrations. It is expected that yields for this VOC fraction will improve substantially by substituting the existing cryo-trap with a Russian Doll trap.<sup>1</sup> A subsequent separation of *HVP-VOCs* from the CO<sub>2</sub> fraction will require a preparative gas chromatographic step that has not yet been developed.

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## INTRODUCTION

It is well known that atmospheric volatile organic compounds (VOCs) play an important role in urban ozone ( $O_3$ ) formation during the summer through a complex series of reactions that include nitrogen oxides ( $NO_x$ ) and sunlight. It is believed that these same mechanisms may be responsible for high levels of  $O_3$  found over the South Atlantic as a result of VOCs,  $CO$ , and  $CH_4$  produced from urban pollution and biomass burning in South America and Africa.<sup>2</sup> For effective strategies to control urban  $O_3$ , it is necessary to obtain a reliable assessment of the relative contributions of natural and anthropogenic VOCs in the atmosphere<sup>3</sup>. One approach to the source apportionment of atmospheric VOCs requires radiocarbon ( $^{14}C$ ) measurement of this fraction separated from ambient air. Radiocarbon measurements of separated VOCs would give a quantitative measure of biogenic ( $^{14}C/^{12}C=10^{-12}$ ) and fossil ( $^{14}C/^{12}C=0$ ) carbon contributions to this fraction. To address this need, a gas separation (GS) system has been developed at the National Institute of Standards and Technology (NIST) for the simultaneous separation of VOCs with relatively low vapor pressures (*LVP-VOCs*), *ca.* *n*-decane and above with a vapor pressure  $\sim 0.1$  Pa or lower, and  $H_2O$ , VOCs with relatively high vapor pressures (*HVP-VOCs*), *ca.* *m*-xylene and below with a vapor pressure  $\sim 0.1$  Pa or higher, and  $CO_2$ ,  $CO$  and  $CH_4$  from ambient air through sequential cryogenic separation and selective oxidation techniques. Typical concentrations of these compounds (or chemical classes) and the amount of carbon expected from each fraction by processing  $0.1$  m<sup>3</sup> of air at  $20$  °C and 100% humidity are given in Table 1. Subsequent to this bulk separation, a pure *HVP-VOC* fraction would be obtained by preparative (prep) gas chromatographic separation of this fraction from the sample  $CO_2$ . Given that this approach of isolating VOCs for carbon isotope measurements is successful, the method could be applied to VOCs from remote areas to address issues such as biomass burning as mentioned above.

A preliminary evaluation of the entire measurement process that will lead to  $^{14}C$  measurements of volatile organic carbon fraction (VOC fraction) is reported here. Important issues that are addressed include: 1) the ability to isolate a pure VOC fraction from all other gaseous carbonaceous species, 2) the chemical identity of this VOC fraction, 3) the level of contamination (blank), 4) the recovery efficiency, and 5) the accuracy of  $^{14}C$  accelerator mass spectrometry (AMS) measurements at the 20 microgram carbon level. These variables are important to quantify and control so that reliable  $^{14}C$  measurements of VOC fractions can be made and interpreted in terms of biogenic and fossil carbon contributions to an urban airshed.

A method for the separation of  $CO$  and  $CH_4$  from  $0.1$  m<sup>3</sup> of whole air for  $^{14}C$  measurement<sup>4</sup> has been modified for this study to include the separation of VOCs. The separation method for  $CO$  and  $CH_4$  had been applied to wintertime samples collected in Las Vegas, NV and Albuquerque, NM.<sup>5,6</sup> The results showed a depletion in  $^{14}C$  relative to the activity of modern carbon (*ca.*  $1 \times 10^{-12}$   $^{14}C/^{12}C$ ) which suggested that both wood burning and motor vehicle emissions contributed significantly to the excess  $CO$  and  $CH_4$  concentrations in these samples. This is an example of how isotope measurements of specific compounds or classes of chemical species have been applied to apportion sources of urban pollution. Similarly, it is expected that  $^{14}C$  measurements of VOC fractions from metropolitan areas during the summertime will provide a direct measure of fossil and biogenic VOC contributions and thus allow for more accurate assessments of the role that anthropogenic and natural processes play in the formation of  $O_3$ .

The purpose of this paper is to summarize our current capabilities to separate atmospheric VOCs from  $0.1$  m<sup>3</sup> of ambient air for  $^{14}C$  measurement. Although the GS system is also designed to separate  $CO_2$ ,  $CO$  and  $CH_4$ , discussion will focus only on VOCs. Information about these other carbonaceous species will be included only as they pertain to steps taken to isolate a pure VOC fraction, void of any significant contamination. The omission of these species in this discussion does not suggest that  $^{14}C$  measurements of  $CO_2$ ,  $CO$  and  $CH_4$  are unimportant, because they may provide additional source information necessary for accurate interpretation of the  $^{14}C$ -VOC measurements. A more complete discussion of the GS system that would include the ability to separate

the other carbonaceous species is beyond the scope of this discussion.

## EXPERIMENTAL SECTION

The GS system and separation protocol are being evaluated for contamination (blanks) and recovery of the VOC fractions by processing NIST "primary" standards, NIST Standard Reference Materials (SRMs), zero air, helium, and *real* ambient air samples. The air samples were collected during August, 1990 in Atlanta, GA, as part of the U.S. EPA Ozone Precursor Study.<sup>7</sup> The results from these experiments allow for close scrutiny of the sample collection, chemical separation, and sample oxidation processes. The method of preparing Fe-C targets with microgram ( $\mu\text{g}$ ) carbon quantities for AMS  $^{14}\text{C}$  measurements has been developed by Verkouteren et al.<sup>8</sup> and validated by Klouda et al.<sup>9</sup> From the exploratory work on VOCs reported here, our plan is to establish an effective protocol for the following: 1) separation of the VOC fraction from  $\text{CO}_2$ , CO and  $\text{CH}_4$ , 2) quantitative recovery of VOCs as  $\text{CO}_2$ , and 3) minimal contamination. These stages of chemical preparation are important to control to obtain reliable measurements of the  $^{14}\text{C}$  abundance of atmospheric VOCs.

### Apparatus for Collecting Ambient Air

A prototype field sampling system was designed to collect an ambient integrated fine-particulate sample on a quartz-fiber filter and an air sample compressed in a 32-Liter SUMMA<sup>®</sup> polished stainless-steel canister. The filtering apparatus used a cyclone impactor, operated at *ca.* 10 Liters per minute (L/min), to remove the coarse ( $> 2 \mu\text{m}$  dia) and fine ( $< 2 \mu\text{m}$  dia) particles from the air stream while loading the fine particles on a quartz-fiber filter. All volumes and flow rates are reported at STP, 101 kPa and 273 K. Air was tapped from the sampling line downstream from the filter and directed to a second system to obtain an integrated air sample corresponding to the same time period as the filter sample. While maintaining a constant flow with a 0-2 L/min flow controller, pre-filtered air was compressed to a final sample pressure of 303 kPa (3 atmospheres) in the pre-evacuated canister. The system was later modified to function under field conditions which included an environmental enclosure and an on-line bleeder valve for clearing the system line of accumulated water as a result of high humidity and temperature conditions.<sup>10</sup> Seven ambient air samples were collected during August 1990 in Atlanta, GA, using this sampling protocol.<sup>10</sup> Some important issues with regard to sample collection and storage include: 1) potential loss of VOCs through the blow-off valve designed to remove any water that may clog the sample line, 2) possible sample contamination due to storage in canisters for extended periods of time, and 3) stability of compounds, in particular oxygenates, in canisters. These questions are intended to be addressed at a later time.

### Reference Gas Mixtures

Reference gas mixtures with known chemical compositions were used to evaluate the *LVP-VOC/H<sub>2</sub>O* fraction and the *HVP-VOC/CO<sub>2</sub>* fraction (For brevity in the following, the labels for these fractions may not include " $\text{H}_2\text{O}$ " or " $\text{CO}_2$ ", depending on the context). One such mixture was made by diluting to ambient (nanomole/mole level) hydrocarbon concentrations a natural gas sample containing eight hydrocarbons ( $\text{C}_1\text{-C}_8$ ) of known chemical composition; five of the eight hydrocarbons had also been analyzed for their  $^{13}\text{C}/^{12}\text{C}$  abundance. The diluent (balance) zero air was Scott Specialty Gases Ultra Zero Ambient Monitoring (UZAM) air containing  $\text{CO}_2$  at ambient concentrations (*ca.* 370 micromole/mole) in air. The presence of  $\text{CO}_2$  in this mixture enabled us to evaluate the system for separating  $\text{CO}_2$ ,  $\sim 17.5 \text{ mg C}$ , from *LVP-VOCs*,  $\sim 30 \mu\text{g C}$ ; the amounts expected from  $0.1 \text{ m}^3$  of air. The fact that  $\text{CO}_2$  was already in the balance gas made it possible to reach the target concentrations for all species in the final mixture by a simple two-stage dilution. Although the total VOC concentration of the natural gas reference mixture was too low for evaluating the VOC recovery, the material was useful for determining the blank for the separation of the *LVP-VOC* fraction from  $\text{CO}_2$ , CO, and

CH<sub>4</sub>. For future separation and recovery experiments, natural gas samples with known isotopic composition will be diluted with UZAM air to produce  $\mu$ mole/mole levels. In addition, two separate NIST "primary" standards were used to evaluate the efficiency of the separation process: #8363 containing C<sub>2</sub>-C<sub>3</sub> hydrocarbons in air and #8392 containing C<sub>6</sub>-C<sub>10</sub> hydrocarbons in N<sub>2</sub> at nanomole/mole concentrations.

### System and Procedure for Gas Separations

**System Characteristics.** The gas separation system is designed to separate simultaneously the following chemical fractions from 0.1 m<sup>3</sup> whole air: 1) *LVP-VOCs* and H<sub>2</sub>O, 2) *HVP-VOCs* and CO<sub>2</sub>, 3) CO oxidized to CO<sub>2</sub>, and 4) CH<sub>4</sub> oxidized to CO<sub>2</sub> (Figure 1). The lower half of the system is the sample processing section made of glass tubing with primarily glass valves. This section contains flow controllers, traps for collecting condensable gases at cryogenic temperatures, a packed column of Schutze Reagent (I<sub>2</sub>O<sub>5</sub> on silica gel) to oxidize CO to CO<sub>2</sub> at room temperature, and a packed column of Pt on alumina pellets operated at 830 °C to oxidize CH<sub>4</sub> to CO<sub>2</sub>. The flow controllers, limited by the manufacturer's reported precision of 1%, are calibrated for accuracy against a Calflow mercury piston and the NIST mercury piston standard.

The upper half of the system is made entirely of stainless-steel high vacuum fittings and valves for manometry of microliter (micro-line) and milliliter (macro-line) volumes of gas. The micro-line, for manometry of VOCs, CO, and CH<sub>4</sub>, oxidized to CO<sub>2</sub>, uses a 13.3 kPa (100 Torr) pressure transducer and a calibrated volume of 23.3 ± 0.3 mL at 23 °C. All uncertainties reported are 95% confidence limits. The macro-line, for manometry of the *HVP-VOC/CO<sub>2</sub>* fraction, uses a 133 kPa (1000 Torr) pressure transducer with a calibrated volume of 69.5 ± 1.1 mL at 23 °C. The confidence intervals reported for these manometer volumes are dominated by a long term (months to years) uncertainty in the behavior of the pressure transducers. [It is likely that these volume errors can be reduced by periodic calibration using a single flask volume which has been precisely calibrated (± 0.005%) using H<sub>2</sub>O.] Each manometer system is contained in an individual Plexiglas® "adiabatic box" to control the temperature during the pressure measurement for subsequent calculation of the gas volume using the ideal gas law. The pressure transducers are calibrated at NIST using a medium-range ultrasonic interferometer manometer.<sup>11</sup>

**Separation Procedure.** A reference gas mixture or ambient air sample, previously analyzed for gas composition, is adapted to one of the two inlet ports (I1 or I2) of the GS system (Figure 1). For most experiments, inlet I1, with a 0-5 L/min flow controller, is used at a flow of 0.5 L/min. The 0-200 cm<sup>3</sup>/min flow controller is used only for processing He when evaluating the possibility of system contamination or for on-line dilution of NIST high concentration ( $\mu$ mole/mole) SRMs. Prior to processing, the entire gas separation line up to the canister valve is first evacuated with the roughing pump (bottom center of Figure 1), then with the turbo molecular pump (top-center, Figure 1) to lower than 0.1 Pa (1 mTorr). Next, the three valves for each of the four cryo-traps are closed and the traps are reduced to their respective operating temperatures. Trap #1, which isolates the *LVP-VOCs* and H<sub>2</sub>O is maintained at -80 °C to -90 °C with an ethanol/dry ice/liquid nitrogen slurry. However, given the flow rate, trap design, and unpacked trap, the actual temperature of the gas stream at the outlet of the trap averages around -70 °C for the cryogen at -85 °C. Trap #2, which collects the combined *HVP-VOCs* and CO<sub>2</sub>, is operated at -196 °C with liquid nitrogen. Similarly, the sample air stream at the outlet to the liquid nitrogen trap, under processing conditions, runs about -170 °C. Trap #3, which recovers CO<sub>2</sub> from the selective oxidation of CO over Schutze Reagent at room temperature, is operated at -196 °C. Finally, trap #4, which collects CO<sub>2</sub> and H<sub>2</sub>O from the high temperature (ca. 830 °C) catalytic oxidation of CH<sub>4</sub> to CO<sub>2</sub> in the presence of oxygen (O<sub>2</sub>), is maintained at -196 °C. Prior to actual processing of SRMs and reference materials, the flow rate is established through a three-way valve just downstream of the flow controller. For samples, where virtually the entire volume is to be processed, the flow rate is not established prior to processing. At this point, the trap isolation valves are opened and the gas is introduced to the system for processing.

The cryo-traps were designed with loops that pass in and out of the cryogen to avoid losses due to the formation of aerosols from the condensation process. Sections of the cryo-traps outside the cryogen were heated enough to avoid subambient cooling due to the cryogen vapor. Since the automatic liquid nitrogen filling process produced excessive N<sub>2</sub> vapor during filling, it was necessary to occasionally heat the outside coils as high as 100-150 °C to avoid cooling below ambient conditions. This lack of temperature control was likely the cause of an observed inefficiency in collecting all the atmospheric CO<sub>2</sub> in trap #2 which resulted in a CO<sub>2</sub> contamination of the CO fraction in the Atlanta samples. By replacing trap #2 with a Russian Doll trap, collection efficiencies for CO<sub>2</sub> are expected to improve to 100%. Additionally, the efficiency of trap #1 may have been affected by poor control of the heated portion of the trap outside the cryogen. In the future, this trap will be packed with deactivated glass wool with better control of the heated portion of the trap in an attempt to improve the efficiency.

Following the separation process, the inlet is closed and the system is pumped to high vacuum using the roughing pump, then the turbo molecular pump as before. The trap isolation valves are then closed, and the condensable gases from traps #2, #3, and #4 are individually cryo-transferred to the appropriate section of the upper manifold for manometry to calculate recoveries for each fraction. The sample fractions, as CO<sub>2</sub>, are then transferred to individual Vycor break-seals for storage to await the preparation of AMS targets for <sup>14</sup>C analysis. Since it is not possible to get an accurate manometric measurement of the LVP-VOC fraction in the presence of 1 mL of H<sub>2</sub>O, this composite fraction is expanded into a heated (80 °C) portion of the processing line just to the right of the trap and completely condensed at -196 °C in a Vycor break-seal for sealing and storage to await oxidation to CO<sub>2</sub>. As a measure of recovery, the volume measurement of each fraction, except for the LVP-VOC/H<sub>2</sub>O fraction, is compared to the expected volume determined for the class of compounds in the canister or cylinder based upon concentration and sample volume. For *real* ambient samples, the mass of air processed and the ambient air density are used to calculate the volume of air processed. Hydrocarbon concentrations are determined by gas chromatography (GC) with flame ionization detection (FID).

To a first approximation, VOCs are condensed in traps #1 and #2 according to their vapor pressures<sup>12</sup> under processing conditions. As such, the VOC fractions are operationally defined as LVP-VOC (trap #1) and HVP-VOC (trap #2) fractions. This somewhat crude separation step is designed to separate compounds having higher boiling points from those having lower boiling points. This bulk separation should make it easier to purify the HVP-VOC fraction from sample CO<sub>2</sub> using prep GC prior to oxidation of this VOC fraction. The two VOC fractions would then be combined for a single <sup>14</sup>C measurement.

### Evaluation of the Separation Process

Composition of LVP-VOC/H<sub>2</sub>O and HVP-VOC/CO<sub>2</sub> Fractions. Recoveries are studied by determining the volumes and the chemical compositions of LVP-VOC/H<sub>2</sub>O and HVP-VOC/CO<sub>2</sub> fractions separated from *dry* "primary" standards and *wet* ambient samples. Following the separation of these materials, the total condensed volume is determined by manometry and then transferred to a break-seal vial for storage to await chemical analysis. Subsequently, the condensates are transferred *in vacuo* from their break-seal storage containers to a GC loop at -196 °C for injection on column. The column is a Chrompack fused silica open tubular column, 25 m x 0.53 mm ID coated with a 10µm film thickness of Al<sub>2</sub>O<sub>3</sub>/KCl (PLOT) operated under the following conditions: 45 °C for 10 min, 10 °C/min to 200 °C and hold, 3 mL/min carrier flow rate, 30 mL/min make-up N<sub>2</sub>, and FID at 250 °C. For calibration of the GC/FID, NIST "primary" standards were cryogenically preconcentrated at -196 °C in the GC loop at a flow of 75 mL/min for 3.3 min, equal to a total injection volume of 250 mL. GC/FID analysis of the LVP-VOC/H<sub>2</sub>O fraction from the ambient samples will require purge and trap techniques for injection on a DB column. The remaining H<sub>2</sub>O will be analyzed for compounds that may be completely soluble

in H<sub>2</sub>O. This approach provides quantitative yield information from measured concentrations of small volumes ( $\mu\text{L}$ -mL) of gases, except for possibly a few very light hydrocarbons, e.g., ethane, that may exhibit loss during the transfer to the loop, even at -196 °C.

The composition of blank condensates are measured by quadrupole mass spectrometry (QMS) and GC/FID. The extent that CO<sub>2</sub> is entrained in the *LVP-VOC*/H<sub>2</sub>O fraction is quantified by allowing the liquid H<sub>2</sub>O to equilibrate with its vapor in a laser cell while measuring the CO<sub>2</sub> concentration by diode laser IR absorption analysis. This latter technique is non-destructive allowing for the quantitative re-recovery of the *LVP-VOC*/H<sub>2</sub>O fraction.

Volume of CO<sub>2</sub> from the Oxidation of *LVP-VOC*s. Subsequent to the separation process, the combined *LVP-VOC*/H<sub>2</sub>O fraction is subjected to two freeze-thaw cycles in an attempt to separate CO<sub>2</sub> that may have been dissolved or entrained in this fraction during separation. The procedure involves the quantitative transfer of the *LVP-VOC*/H<sub>2</sub>O fraction from the break-seal to the vacuum line *via* a metal bellows. A vacuum is drawn on the break-seal, the tube cracked, and the fraction is transferred quantitatively at -196 °C to a cold finger just to the right of the micro-line adiabatic box in Figure 1. The fraction is then warmed to -78 °C for 5-10 minutes at which point any CO<sub>2</sub> occupying the head space is condensed at -196 °C in the calibrated volume for manometric measurement.

The oxidation of the *LVP-VOC* fraction is accomplished by first cryo-transferring the contents of this fraction from the break-seal to trap #3. Then, the pre-evacuated trap #4, used previously for collecting CO<sub>2</sub> derived from the oxidation of CH<sub>4</sub> during the separation process, is reduced to -196 °C and opened to the vacuum system on the right in Figure 1. With the temperature of the Pt/Al catalyst at ~830 °C, ultra-high purity (UHP) O<sub>2</sub> (99.99%) is introduced at 0.1 L/min through the I1 inlet, through traps #2 and #3 while at -196 °C, bypassing the Schutze Reagent (I<sub>2</sub>O<sub>5</sub>), and flowing up to trap #3 containing the *LVP-VOC*/H<sub>2</sub>O fraction. By opening trap #3 valves (bypass valve closed), O<sub>2</sub> begins to flow through the trap, through the catalyst and into trap #4. After approximately 3 min, the pressure in the system reaches ca. 13.3 kPa (< 100 Torr) at which time the left valve to trap #4 is opened to the roughing pump to draw the *LVP-VOC*/H<sub>2</sub>O fraction completely through the catalyst for oxidation with subsequent trapping of the combustion products plus water in trap #4. This takes approximately 10 minutes and is estimated to use ca. 1 Liter of UHP O<sub>2</sub>. Once all the *LVP-VOC*s are combusted to CO<sub>2</sub> and collected along with the water in trap #4, the O<sub>2</sub> source is closed and the residual O<sub>2</sub> is evacuated from the processing line. This total condensate is then quantitatively cryo-transferred using liquid nitrogen to a cold finger just to the right of the micro-line adiabatic box for distillation of the CO<sub>2</sub> from the H<sub>2</sub>O followed by volumetric determination of the CO<sub>2</sub>. The blank for this oxidation procedure is evaluated by processing a "no sample" under identical conditions to that of a *LVP-VOC* fraction.

The recovery efficiency for separating the *LVP-VOC* fraction from ambient air samples is evaluated by comparing the calculated mass of carbon from the measured volume of CO<sub>2</sub> recovered from the oxidation of this VOC fraction to the expected mass of carbon. The expected mass of carbon is based on the volume of air processed and the total *LVP-VOC* concentration (as nanomole C/mole) measured in the original air sample from the canister. GC/FID analyses are performed on the air samples by pre-concentration of 250 mL of gas at liquid Ar temperature prior to injection onto a DB-1 capillary column.

#### AMS Fe-C Target Preparation and <sup>14</sup>C Measurement

Iron-carbon targets for AMS <sup>14</sup>C measurement are prepared by the Fe catalyzed method for reduction of CO<sub>2</sub> to graphitic carbon.<sup>13</sup> This method has been modified by Verkouteren and coworkers<sup>8,14</sup> for small

(microgram carbon) samples by using hot Zn, replacing Fe powder with Fe wool, and including H<sub>2</sub> to minimize CO recombination thereby reducing CO<sub>2</sub> to graphitic carbon directly on the Fe wool. Finally, the Fe-wool/Carbon matrix is fused in an inert atmosphere to a solid solution (bead). The iron serves as a carrier for the reduced carbon and is believed to be less susceptible to contamination. This "closed-system" technique has been applied to several studies with sample sizes as small as 16 µg C.<sup>9</sup>

The <sup>14</sup>C/<sup>13</sup>C ratio measurements of NIST SRMs as Fe-C beads are performed on the University of Arizona tandem accelerator mass spectrometer. The measurement sequence or "run" consists of cycling 8 times between <sup>14</sup>C (40 s) and <sup>13</sup>C (4 s). The mean <sup>14</sup>C count rate is divided by the mean <sup>13</sup>C count rate for each run. The number of runs varies from 4 to 16 per target. This procedure is applied to as many as 32 targets per target-wheel, generally 26 samples and 4 oxalic acid standards for radiocarbon dating, NIST SRMs 4990B and 4990C and 2 NIST RM21 Graphites. The NIST RM21 Graphite is included as a third standard to quantify the amount of modern carbon contamination. Additional details regarding the instrument and further discussion of the procedures are reported elsewhere<sup>15</sup>. Replicate measurements of the <sup>14</sup>C/<sup>13</sup>C ratio obtained from the same target are pooled by calculating a weighted mean and 1σ-Poisson standard error. The current AMS <sup>14</sup>C measurement sensitivity for modern carbon as an Fe-C bead is 20 µg-C at the 1.4% precision based on counting statistics.<sup>9</sup> Results of RM21 Graphite and SRM 4990B Oxalic Acid measurements show that contamination due to the reduction chemistry for preparing targets is 1.0 ± 0.5 µg of modern carbon for samples in the 20-50 µg C range.

## RESULTS AND DISCUSSION

A series of exploratory experiments was performed on the NIST GS system to evaluate its capabilities and a proposed procedure to isolate VOCs from 0.1 m<sup>3</sup> of ambient air. At the outset, it was believed that the blank, representative of the entire measurement process, would likely be significant since the amount of total carbon recovered from the VOC fraction was estimated at around 50 µg C (see Table 1). As a result, experiments were designed to minimize and control the blank. For blanks that were significant, the material was retained in break-seals for manometric, chemical, and, whenever possible, isotopic measurements. The recovery of VOCs was also studied by processing hydrocarbon standards to evaluate the degree of separation and yield.

### Blank Evaluation

Since the method presented for separating and converting VOCs to a suitable chemical form for AMS <sup>14</sup>C measurements requires multiple chemical steps, a thorough examination of the entire process blank is essential. The following blanks associated with the *LVP-VOC* fraction are under investigation: 1) the *system blank*, a result of the interaction of the sample with the GS system and Vycor break-seals, 2) entrainment of sample CO<sub>2</sub> (cross-contamination) in the water (ice) lattice, and 3) the oxidation blank for the combustion of VOCs to CO<sub>2</sub>. The AMS target preparation blank, mentioned in the experimental section, has been evaluated separately and will be reported elsewhere.<sup>9</sup> Preliminary results of experiments related to the blank for the *LVP-VOCs* are summarized below.

*LVP-VOC Fraction Blanks*. Reagent helium, a natural gas sample diluted to nanomole/mole concentrations, CO diluted to the µmole/mole level, and Atlanta samples (Table 2) were processed to assess the overall blank contribution to the *LVP-VOC* fraction. These reference materials included the following characteristics: 1) the He was expected to be virtually free of all fractions of interest, 2) the natural gas mixture contained C<sub>2</sub>-C<sub>6</sub> hydrocarbons, CH<sub>4</sub> and CO<sub>2</sub> at or near ambient concentrations, 3) the CO mixture also included ambient CO<sub>2</sub>, and 4) the ambient samples were chemically characterized. All but the ambient samples were processed under dry conditions. By processing 0.1 m<sup>3</sup> of these materials, blank contributions were evaluated. Analysis of the trapped condensates were made by manometry, semi-quantitative gas analyses by QMS, GC/FID analysis, and

diode laser IR absorption measurements. All blank quantities reported below are in units of  $\mu\text{L}$  at STP and, for those fractions that have been chemically characterized,  $\mu\text{g C}$  has been included.

The system blank was estimated by processing pure He. The average total volume of condensate recovered from trap #1 (*LVP-VOC* fraction), determined by manometry, was  $1.2 \pm 1.0 \mu\text{L}$ . Of the three replicate system blanks, QMS results of one experiment showed that 95% of the  $0.98 \mu\text{L}$  recovered was  $\text{H}_2\text{O}$ , the other 5% was identified as  $\text{CO}_2$ . This would amount to a  $0.05 \mu\text{g C}$  system blank ( $0.1 \mu\text{L}$ ). If the gas composition from this single experiment was representative of the gases from the other two experiments, then the effects of processing and storage would not influence the final result in a significant way, assuming of course that this carbon is of modern activity which has been our past experience. Even if one assumes that the total blank volume recovered was  $\text{CO}_2$ , this amount of carbon contamination,  $0.6 \pm 0.5 \mu\text{g C}$ , would be relatively small (*ca.* 2.6%) contribution to the total sample carbon expected (*ca.*  $25 \mu\text{g C}$ ).

Next, the possibility of sample  $\text{CO}_2$  cross-contamination, while condensing the *LVP-VOCs*, was examined by processing  $0.1 \text{ m}^3$  of the natural gas mixture which contained  $\text{CO}_2$  at ambient levels. From this experiment, a total volume of  $1.8 \mu\text{L}$  was expected given that the combined concentration of the heaviest hydrocarbons ( $\text{C}_7$ 's and  $\text{C}_8$ 's) in the mixture amounted to 18 nanomole/mole and assuming 100% trapping efficiency. Later, it was realized that this expected volume would represent an upper limit since compounds with vapor pressures as low as  $\sim 0.1 \text{ Pa}$  ( $1 \text{ mTorr}$ ) were only partially retained at  $-80 \text{ }^\circ\text{C}$  to  $-100 \text{ }^\circ\text{C}$ . Of the total condensate from trap #1, QMS analysis showed that 94-97% was  $\text{H}_2\text{O}$ . The other few percent was identified as  $\text{CO}_2$ , which amounted to  $0.3 \pm 0.5 \mu\text{g C}$ . This estimate also included the system blank effect reported above.

The effect of  $\text{CO}_2$  cross-contamination was also explored by subjecting three Atlanta *LVP-VOC/H}\_2\text{O}* fractions, GT5, GT6, and GT7, to two freeze ( $-196 \text{ }^\circ\text{C}$ ) and thaw ( $-80 \text{ }^\circ\text{C}$ ) cycles to remove any possible  $\text{CO}_2$  from these fractions. Each fraction was individually treated by adapting the break-seal containing the *LVP-VOC/H}\_2\text{O}* fraction to the vacuum line by way of a metal bellows such that a vacuum could be established around the tube. The freeze/thaw procedure was performed as previously outlined. After a thawing for a period of 5-10 minutes at  $-80 \text{ }^\circ\text{C}$ , the total volume of head-space gas, assumed to be  $\text{CO}_2$ , was at most  $0.03 \pm 0.01 \mu\text{L}$  of gas (or  $0.02 \pm 0.01 \mu\text{g C}$ ). It was later suggested that this estimate would be a lower limit since the  $\text{CO}_2$  equilibrium between liquid and gaseous water would not have been established within the sampling period; it was estimated that equilibrium would be established after about 24 hours.<sup>16</sup> Therefore, any  $\text{CO}_2$  present would have remained in solution. Given the solubility of  $350 \mu\text{mole/mole}$   $\text{CO}_2$  in equilibrium with water at  $0 \text{ }^\circ\text{C}$ , the lowest temperature at which the solubility constant has been measured, the estimated volume of  $\text{CO}_2$  in the liquid would have been about  $0.6 \mu\text{L}$  (or  $0.3 \mu\text{g C}$ ).

A more direct means of measuring  $\text{CO}_2$  cross-contamination in the *LVP-VOC/H}\_2\text{O}* fraction was investigated using the non-destructive technique of Diode Laser IR second derivative absorption analysis. A sample was introduced into a  $74.8 \text{ cm}$  path length cell with a cell volume of  $294.8 \text{ mL}$ , the total volume of the system of  $427.1 \text{ mL}$ , via a break-seal containing the *LVP-VOC/H}\_2\text{O}* fraction, adapted as described above, and held at ice bath temperature. The break-seal was then cracked introducing water vapor into the system until a pressure of  $613 \text{ Pa}$  ( $4.610 \text{ Torr}$ ) was reached, i.e. the vapor pressure of  $\text{H}_2\text{O}$  at about  $0.2 \text{ }^\circ\text{C}$ . Next, the concentration of  $\text{CO}_2$  was measured periodically over 24 h while the system was approaching equilibrium. Measurements of  $\text{CO}_2$  concentration were made on Atlanta GT2 and GT3 samples relative to a NIST SRM  $\text{CO}_2$  in air certified at  $351.2 \mu\text{mole/mole}$ . Average  $\text{CO}_2$  concentrations measured at equilibrium represent  $\sim 1 \mu\text{g C}$  contamination from  $\text{CO}_2$  (Table 3). Henry's Law constant for the equilibrium of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  at  $0 \text{ }^\circ\text{C}$ ,  $-\log K = 1.1 \text{ moles-Liter}^{-1}\text{-atm}^{-1}$ ,<sup>17</sup> was used to calculate the amount of  $\text{CO}_2$  remaining in the liquid at equilibrium, approximately 2 orders of magnitude less than that in the gas phase. The median value of carbon contamination

measured in these two experiments,  $0.9 \mu\text{g C}$ , has been applied to the correction of the sample (*LVP-VOC*) carbon for yield purposes.

The final blank studied was for the oxidation of the *LVP-VOC* to  $\text{CO}_2$ . Given the oxidation procedure outlined in the experimental section, the blank was estimated by performing a series of combustions with "no sample" present. The average total volume of condensate collected from these combustion runs following distillation from  $-78 \text{ }^\circ\text{C}$  was  $2.7 \pm 1.5 \mu\text{L}$ . Blank results from the oxidation of  $\text{CH}_4$  using this same catalyst suggested that this blank would be predominantly  $\text{CO}_2$ . Assuming this to be the case, the oxidation step would contribute  $1.5 \pm 0.8 \mu\text{g C}$ . Therefore the combined system and  $\text{CO}_2$  cross-contamination blank ( $0.9 \mu\text{g C}$ ) plus the oxidation blank ( $1.5 \mu\text{g C}$ ) yield an overall *LVP-VOC* blank of  $2 \pm 1 \mu\text{g C}$ .

***HVP-VOC Fraction Blanks.*** The experiments that involved the processing of He, as mentioned above for the *LVP-VOC* blank, were also used to evaluate the system blank for the condensation of the *HVP-VOC/CO*<sub>2</sub> fraction during the bulk separation process. The total condensates recovered from these experiments that would represent the effect of cryo-trapping this fraction were 7.2, 14.8, and 18.4  $\mu\text{L}$ . These blank volumes represent an upper limit of  $13.5 \pm 14.2 \mu\text{L}$ , since the He alone may contain trace level impurities of  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , and hydrocarbons and the chemical composition of this condensate was not determined. If one assumes that  $\text{CO}_2$  is the largest impurity, then the estimated blank would be equivalent to  $7 \pm 8 \mu\text{g C}$ .

The final phase necessary for isolating a pure *HVP-VOC* fraction will require prep GC separation of sample  $\text{CO}_2$  from this material followed by oxidation of the purified *HVP-VOC* fraction to  $\text{CO}_2$ . An alternative approach to Prep GC to obtain a pure VOC fraction may be to preprocess the air from the canister with a LiOH denuder<sup>18</sup> followed by complete condensation of the air at  $-196 \text{ }^\circ\text{C}$  into another canister. The *HVP-VOCs* would then be separated from whole air using the NIST GS system. Success of this latter method would greatly depend on the denuder efficiency, the chemical blank, and whether losses of VOCs occur during the process. If VOCs are lost during the process, these compounds and their efficiencies must be quantified for an accurate interpretation of <sup>14</sup>C measurements. It is believed that *some oxygenated compounds are less likely to survive the denuder step than are the hydrocarbons.*<sup>19</sup> Thus, while the original objective was to measure the <sup>14</sup>C abundance of the total VOCs, the final *HVP-VOC* fraction may be dominated by the unreacted (primary) light VOCs. If the denuder is effective at removing the  $\text{CO}_2$  to an acceptable level, 1 part in  $\sim 10^5$ , but also removes oxygenates in the process, then a <sup>14</sup>C measurement of the "primary" VOCs may also contribute to the understanding of source contributions to  $\text{O}_3$  formation.

Currently, the denuder is being evaluated for its ability to remove  $\text{CO}_2$  from moist air and its effect on VOCs at the nanomole/mole level.<sup>19</sup> Also, plans are underway to investigate the feasibility of prep GC for separating  $\text{CO}_2$  from the *HVP-VOC* fraction and chemically characterizing the *LVP-VOC/H*<sub>2</sub>O fraction for oxygenates with the intention of recovering both VOC fractions for isotope measurements.

## Recovery Evaluation

Recoveries of VOCs from the separation process were evaluated by processing two "primary" hydrocarbon standards,  $\text{C}_2\text{-C}_8$  (#8363) with concentrations from 15-25 nanomole/mole and  $\text{C}_6\text{-C}_{10}$  (#8392) with concentrations from 26-124 nanomole/mole, plus two Atlanta ambient samples (GT5 and GT6). For the hydrocarbon standards, recoveries for both the *HVP-VOC/CO*<sub>2</sub> and the *LVP-VOC/H*<sub>2</sub>O fractions were obtained by comparing measured hydrocarbon concentrations in each fraction to their expected concentrations. Only Atlanta samples were used to determine the recovery for separation and oxidation of the *LVP-VOC* fraction by

comparing the mass of carbon recovered as CO<sub>2</sub> from the oxidation to the expected mass of carbon from the total concentration of hydrocarbons (in micromole C/mole) expected in this fraction.

Although the Atlanta samples were measured for their chemical composition *after 1.5 years of storage* in canisters at laboratory conditions and the VOC separations took place *six months later*, this long storage period was not of major concern, since one objective of the study was to evaluate the gas separation system and procedure using *real* ambient samples. But, for quality isotope measurements, *sample integrity during the storage must be well characterized*. The GC/FID analyses of the Atlanta samples revealed two unidentified asymmetric peaks in each sample chromatogram that are not normally observed in routine hydrocarbon analysis of ambient samples. Since these peaks represent a substantial portion (37-136 nanomole C/mole) of the total VOC carbon concentration, without identification and quantitation of these compounds their effect on the estimated recovery and integrity of the VOC fractions is not known. If these peaks represent ambient oxygenated compounds, such as acetaldehyde or acetone, the recoveries of these compounds may have been affected by the warm canisters from the field stored under cooler laboratory conditions. Given high humidity, in some cases saturated conditions, some H<sub>2</sub>O would be expected to condense on the canister surface and potentially carry water-soluble VOCs along. Aside from these important but very complex issues, the Atlanta samples afforded a good opportunity to evaluate the measurement process because they represented the actual gas composition of interest.

GC Analysis of HVP-VOC/CO<sub>2</sub> and LVP-VOC/H<sub>2</sub>O Condensates. From the processing of two *dry* hydrocarbon standards, #8363 and #8392, and two Atlanta samples, GT5 and GT6, an aliquot was taken from each *HVP-VOC/CO<sub>2</sub>* fraction and analyzed for gas composition by GC/FID. The recoveries for isolating C<sub>5</sub>-C<sub>8</sub> VOCs in the sample CO<sub>2</sub> were determined by multiplying each concentration by the ratio of the total *HVP-VOC/CO<sub>2</sub>* volume recovered to the total volume of gas processed and dividing by the ambient concentration determined directly from the canister. Assuming that the transfer of an aliquot from the break-seal to the GC loop was complete, *HVP-VOC* recoveries from the processing of #8363, GT5 and GT6 were 27-78% (Table 4). The results for n-hexane from the two ambient samples were in excess of 100% which suggest either a problem with calibration or contamination. Lower *HVP-VOC* recoveries were observed for #8392 which may result from a CO<sub>2</sub> concentration, 2 μmole/mole, 2 orders of magnitude lower than in #8363, GT5 and GT6. The presence of *dry* ice from the CO<sub>2</sub> condensate may be a factor influencing the efficiency for trapping these hydrocarbons considering the cryo-traps were not packed. Losses of these light hydrocarbons from an inefficiency in the cryogenic trapping should become insignificant in the future with the implementation of Russian Doll traps that have been proven to yield 100% recovery for even nanomole/mole concentrations of ethane at -196 °C.<sup>1</sup> If losses occurred during the transfer of the *HVP-VOC/CO<sub>2</sub>* fraction to the GC loop for analysis, then the reported recoveries represent a lower limit.

Recoveries for C<sub>6</sub>-C<sub>10</sub> hydrocarbons in the *LVP-VOC* fraction ranged from 0.01% for benzene to 19% for n-decane. It appears that compounds that have vapor pressures equal to or less than m-xylene or n-decane and have concentrations greater than 25-50 nanomole/mole would be significantly retained in this VOC fraction. To date, only one *LVP-VOC/H<sub>2</sub>O* fraction from an Atlanta sample (GT3), has been analyzed by GC/FID for its gas composition. A ~50 μL aliquot of H<sub>2</sub>O vapor was taken by expanding the head-space gases and liquid H<sub>2</sub>O from the break-seal to a large (~100 mL) volume in the Micro-line section of the GS system (Figure 1) that included 2 break-seals. Once the H<sub>2</sub>O vapor reached ~2.4 Pa (18 Torr), the vapor pressure of water at 24 °C, valves leading to the break seals were closed, the total gas condensed at -196 °C, and the tube flame sealed. Using a PLOT column, GC/FID results of this *LVP-VOC/H<sub>2</sub>O* fraction showed several (*ca.* 25) major peaks below n-decane, but, for the moment, have not been identified. If oxygenated compounds were retained in this fraction, given the GC column used, these compounds were not likely to be resolved and may even be retained.

Future GC/FID and mass selective detection analysis of LVP-VOC/H<sub>2</sub>O fractions from Atlanta samples will be made with a column more suitable for polar compounds and make use of purge and trap techniques to obtain a more representative sampling of this fraction.

LVP-VOC Oxidation Recoveries. Four Atlanta samples were processed and their LVP-VOC fractions oxidized to CO<sub>2</sub> to evaluate the recovery. The yields, corrected for a total process blank, were significantly in excess of the amounts of carbon expected based on hydrocarbons from n-decane and above measured by GC/FID (Table 5). These results raise important concerns regarding the entire chemical process and the means for evaluating the yield. If the GC/FID measurements were an accurate means for evaluating the LVP-VOC recoveries, then the relative amounts of excess carbon prevents one from interpreting the <sup>14</sup>C measurements with any sort of confidence. Alternatively, if the unidentified peaks less than n-decane were condensed in the LVP-VOC/H<sub>2</sub>O fraction, this carbon mass would account for a significant portion of the excess carbon. In addition, some oxygenates may not have eluted from the column and, therefore, would also contribute to this excess carbon mass. AMS <sup>14</sup>C measurements were performed on LVP-VOC fractions from Atlanta samples GT5, GT6, and GT7, but, *until this excess carbon is completely accounted for, the isotope results remain uninterpretable.*

## CONCLUSIONS

Preliminary experiments were performed on a gas separation system developed at NIST by processing 0.1 m<sup>3</sup> of hydrocarbon standards and ambient air samples for the removal of VOCs for isotope (<sup>14</sup>C) measurements. To date, two separate condensates containing VOCs have been isolated: 1) LVP-VOCs condensable at ca. -85 °C, generally those having vapor pressures less than that of n-decane, plus H<sub>2</sub>O and 2) HVP-VOCs condensable at ca. -196 °C, generally those with vapor pressures above that of n-decane, plus CO<sub>2</sub>. Results of the LVP-VOC fraction suggest a blank of  $2 \pm 1 \mu\text{g C}$  and a 19% recovery for n-decane. Gas composition analysis by GC/FID of this fraction isolated from one ambient sample collected in Atlanta, GA detected several compounds below n-decane which have yet to be identified. Masses of carbon recovered from oxidations of four LVP-VOC fractions from Atlanta samples showed an excess carbon that cannot simply be accounted for by the blank. We believe that this excess of carbon may be oxygenated VOCs that are not measured in the original gas composition analysis of the samples.

An upper limit for the HVP-VOC/CO<sub>2</sub> blank has been estimated at  $7 \pm 8 \mu\text{g C}$ , assuming that CO<sub>2</sub> dominates the volume measured. The recoveries of a few select hydrocarbons from this fraction range from 27% to 78% and are variable. The recovery of VOCs in this fraction is expected to improve significantly with the substitution of a Russian Doll trap for cryogenic collection. Investigations are underway to evaluate both preparative GC and a LiOH denuder to separate CO<sub>2</sub> from the HVP-VOCs. In spite of the many difficulties summarized here, isotope measurements of either the total VOC fraction or the two subfractions continues to be a promising approach for determining the biogenic and fossil contributions to VOC precursors of ozone.

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Table 1. Expected volume of gas and mass of carbon of each chemical fraction for 0.1 m<sup>3</sup> air at 20 °C and 100% humidity\*

Chem. Fraction	Concentration [ $\mu$ mole/mole]	Volume [ $\mu$ L]	Mass C [ $\mu$ g]
H <sub>2</sub> O	14,335	1,700	--
CO <sub>2</sub>	360	35,000	17,500
CO	~1	100	50
CH <sub>4</sub>	~2	200	100
VOC*	~1	100	50

\* Estimates based on typical summer concentrations in metropolitan areas. The total non-methane volatile organic compound (VOC) concentration ( $\mu$ mole C/mole) taken from H. Westberg<sup>4</sup> for the summertime in the Baltimore-Washington, DC area. The compound distribution was comprised of 60% paraffins, 30% aromatics, and 10% olefins.

Table 2. Concentration of species in ambient air samples collected during August, 1990 in Atlanta, GA.

Run #	ID #	Date	Time of Day	Concentration [ $\mu$ mole C/mole]			
				VOC	CH <sub>4</sub>	CO	CO <sub>2</sub>
GT1	3992	6	0700-1900	0.56	1.93	0.67	387.3
GT2	3990	8	0700-1900	0.28	1.84	0.81	370.0
GT3	3989	10	0700-1900	0.51	1.88	0.75	364.7
GT4	3995	10-11	1900-0700	1.22	2.59	1.77	426.8
GT5	3991	12	0700-1900	0.52	1.92	0.68	359.6
GT6	3994	13	0700-1900	0.74	1.89	0.76	360.2
GT7	3993	13-14	1900-0700	0.91	2.51	1.08	389.5

\* Total VOC concentrations were obtained from the total area of all peaks detected by GC/FID. Methane, CO and CO<sub>2</sub> concentrations were measured by GC/FID; CO and CO<sub>2</sub> were reduced to CH<sub>4</sub> prior to the FID. Methane concentrations were also measured by diode laser IR absorption. All concentrations are relative to standards under *dry* conditions. Uncertainties are assigned as follows:

VOC - Total VOC, ~5%

CH<sub>4</sub> - <1%, calibrated against SRMs 1658a,1659a,1660a

CO - <7%, calibrated against SRM 2612a

CO<sub>2</sub> - ca. 0.3%, calibrated against SRMs 2609, 1672, and two primary gravimetric standards.

Table 3. Diode laser IR absorption measurements of CO<sub>2</sub> cross-contamination of the LVP-VOC/H<sub>2</sub>O fraction separated from Atlanta samples.

ID #	CO <sub>2</sub> Concentration* [μmole/mole]	Mass C‡ [μg]
GT2	811 ± 24	1.23 ± 0.04
GT3	335 ± 22	0.51 ± 0.05

\* Concentrations of CO<sub>2</sub> measured in 612.6 Pa (4.610 Torr) sample H<sub>2</sub>O<sub>(g)</sub> and VOCs in 427.1 mL at 22 °C in equilibrium with ~1 mL of sample H<sub>2</sub>O<sub>(l)</sub> at 0.2 °C. Uncertainties are 95% confidence limits.

‡ Equivalent mass of carbon calculated from the CO<sub>2</sub> concentration measured in the sample H<sub>2</sub>O<sub>(g)</sub> plus VOCs and the occupied volume.

Table 4. Recovery (percent) of *High Vapor Pressure (HVP) VOCs* trapped with CO<sub>2</sub> and *Low Vapor Pressure (LVP) VOCs* trapped with H<sub>2</sub>O from the gas separation process.\*

Compound	b.p. (°C)	HVP-VOC/CO <sub>2</sub>				LVP-VOC	
		#8363	#8392	GT5	GT6	#8363	#8392
isopentane	27.8			36	49	ND	
n-pentane	36.1			78	75	ND	
n-hexane	68.3	70	10	242	158	0.02	ND
benzene	80.1	72	9	71	62	0.02	0.01
n-octane	125.7	45	6	ND	25	0.2	1.4
toluene	110.6	60	7	72	59	0.1	0.6
m-xylene	139.1	33	4			1.5	16
o-xylene	144.4	27		49		1.8	
n-decane	174.1		ND				19

\* Data from the processing of NIST "primary" standards #8363 (C<sub>2</sub>-C<sub>8</sub>) and #8392 (C<sub>6</sub>-C<sub>10</sub>) plus Atlanta samples GT5 and GT6. Standard #8363 contains hydrocarbons at nominally 20 nanomole/mole and CO<sub>2</sub> at 226 μmole/mole in air. Standard #8392 contains CO<sub>2</sub> at ~2 μmole/mole plus hydrocarbons in N<sub>2</sub> at the following concentrations in nanomole/mole: n-hexane, 123.5, benzene, 102.5, n-octane, 48.2, toluene, 108.3, m-xylene, 47.8, and n-decane, 25.6. ND = not detected, <0.01%

Table 5. Recovery of the *Low Vapor Pressure (LVP) VOC* fraction of Atlanta samples trapped with H<sub>2</sub>O and subsequently oxidized to CO<sub>2</sub>.

ID #	Recovered* [μg C]	Expected** [μg C]	Excess C <sup>‡</sup> [μg C]	Unidentified C <sup>‡‡</sup> [μg C]
GT2	24.6	0.6	24.0	5.2
GT5	22.1	0.4	21.7	11.1
GT6	33.6	1.4	32.2	17.9
GT7	29.6	2.1	27.5	18.6

\* Mass of carbon recovered from the combustion of the *LVP-VOC* fraction to CO<sub>2</sub> corrected for a total blank of  $2 \pm 1$  μg C (95% confidence limit); represents system/CO<sub>2</sub> blank (n=2) and oxidation blank (n=3).

\*\* Expected mass of carbon from all peaks above and including n-decane (identified or not), trap #1 cut off (see text), based on GC/FID analysis of air sample from canister. Concentrations of unidentified peaks are calculated assuming that their response factor and C-stoichiometry are comparable to adjacent identified peaks.

‡ Amount of carbon in excess of that expected for the *LVP-VOC* fraction based on GC/FID analysis.

‡‡ Amount of carbon from unidentified GC peaks that eluted before n-decane; if oxygenated, they may partially account for *Excess C*.

# NIST Gas Separation System

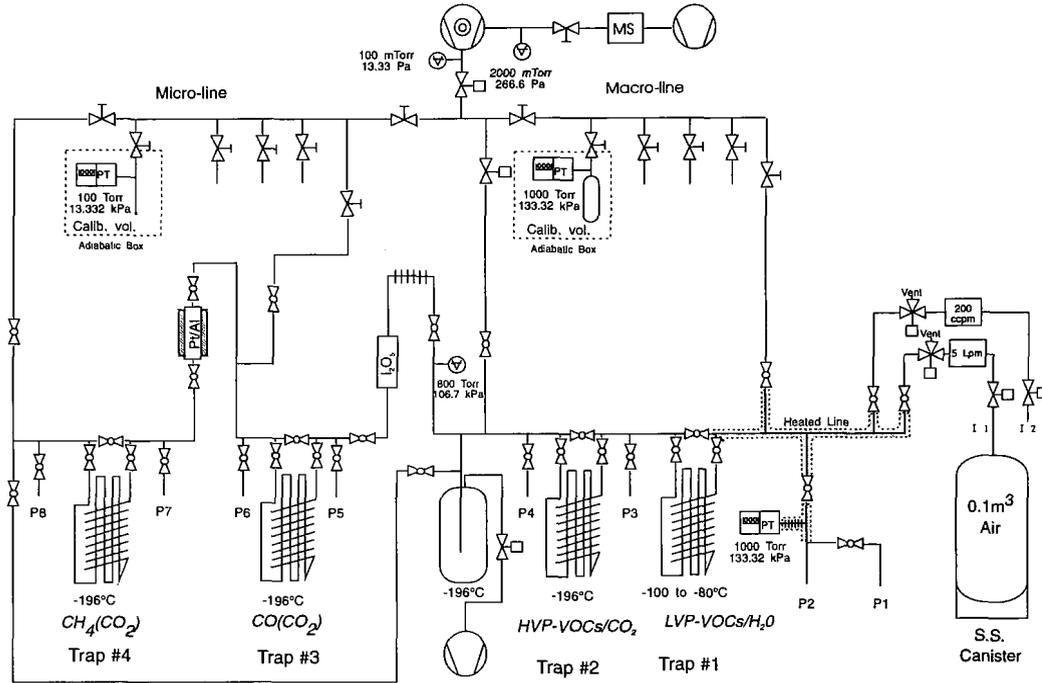


Figure 1. Schematic diagram of the NIST Gas Separation system, lower half of schematic, for the separation of the following fractions: a) Low Vapor Pressure (LVP) VOCs ( $>C_{10}$  for hydrocarbons) and  $H_2O$  in trap #1, b) High Vapor Pressure (HVP) VOCs ( $<C_{10}$  for hydrocarbons) and  $CO_2$  in trap #2, c)  $CO$  (as  $CO_2$ ) in trap #3 and d)  $CH_4$  (as  $CO_2$ ) in trap #4, from whole air. Stainless steel vacuum lines in the upper half of the schematic are for sample distillation and manometric determination in a calibrated volume following separation.

## MONITORING VOLATILE ORGANIC COMPOUNDS (VOCs) IN THE GREEN BAY AREA

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### ABSTRACT

In July 1991, the Wisconsin Department of Natural Resources began operating an urban air toxics monitoring station in the City of Green Bay. The site is a prototype station for a future Wisconsin Air Toxics monitoring network expected to have 4 to 5 sites. Air samples, collected at the station, are analyzed for volatile and semi-volatile organic compounds and for nonvolatile elements. This paper will report on the collection and analysis of the VOCs.

We chose to collect and concentrate VOCs on multi-bed sorbent tubes. After exposure, the VOCs are thermally desorbed from the tube, focused on a second tube and analyzed by gas chromatography with mass spectrometry detection. This paper will report on the following;

1. the choice of the adsorbent tubes and the sampling strategy used with the tubes;
2. the analysis technique used and the incorporation of a pre-analysis nitrogen purge to remove trapped water;
3. the validation of the data collected with comments on the data quality; and
4. a preliminary report on the data collected to date at the monitoring site.

### INTRODUCTION

In July 1991 the Wisconsin Department of Natural Resources, Bureau of Air Management (WDNR-BAM) began the operation of a prototype Hazardous Air Pollutant (Air Toxics) monitoring station in Green Bay. Monitoring at the Green Bay station was designed to be a screening program to determine the concentrations of selected organic compounds (volatile and semivolatile) and inorganic compounds (metals) present in the urban atmosphere. The paper will report on the monitoring conducted for volatile organic compounds which began at the station in August 1991. VOC monitoring was conducted using multi-bed adsorbent tubes to collect the target compounds in the ambient air. After a start-up problem caused by the moisture (water) collected on the sampling tubes was resolved, the routine sampling began operation in November 1991. This paper will discuss the VOC monitoring from November of 1991 to November 1992 and the present state of monitoring operations at the Green Bay station.

### BACKGROUND

The Clean Air Act Amendments of 1991, in Title III, called for the establishment (by the U.S. Environmental Protection Agency) of a network of monitors in major urban areas to measure the concentrations of air toxins due to the myriad of "area" sources in such cities, and to determine the risk of the exposed population. Those sources included such categories as: automobile and truck exhausts; emissions emanating from retail establishments such as dry cleaners and restaurants; household products such as sprays and application liquids, insecticides, rodenticides and herbicides, etc. Some of the specific compounds identified included aromatics, PAHs, POMs, aldehydes, metals, etc.

The WDNR has decided to establish an Urban Air Toxics network to supplement any network to be established by the U.S. Environmental Protection Agency (USEPA) and to determine the risk to populations in cities having the greatest potential of exposure as well as significant numbers of people exposed. In addition, concern

about industrial fugitive emissions in some cities would not be addressed by the USEPA study. The areas in Wisconsin which the WDNR selected for Air Toxics stations include Milwaukee, Superior, central Wisconsin, the Fox River Valley (Oshkosh/Appleton) in addition to Green Bay.

The City of Green Bay was selected as the prototype location because of concern by area citizens, the mix of urban area sources and industrial sources, and a specific request by WDNR local staff. Green Bay is an industrial city located on the southern shore of Lake Michigan's Green Bay and at the mouth of the Fox River, which empties into the bay. The city has a population of approximately 96,500. Industry in the city includes a number of paper mills. Other large air pollution sources in the city include a power plant and a large wastewater treatment facility. The monitoring station was originally located at the WDNR's Bay Beach air monitoring trailer, AIRS No. 55-009-0023, established as a sulfur dioxide monitoring station. The Bay Beach site is located at the north end of the city where predominate southerly winds carry the pollutants. Pollutants measured at the station are emitted by both large and small industries, the power plant, the wastewater treatment plant as well as from automobile and truck traffic.

The prototype monitoring station was intended to collect preliminary data and test sampling methods, with additional monitoring stations to be established in future years. The Green Bay monitoring station and future stations in the Wisconsin air toxics monitoring network are intended to collect data to provide information to be analyzed for potential health risks as well as for ambient concentration trends.

## MONITORING METHODOLOGY

### Sampling

Sampling tubes. Trace organic contaminants in the ambient air, whether toxic or photochemically reactive, can rarely be directly measured. Sampling and analysis methods must often include steps to concentrate compounds of interest prior to the actual analysis. Compound concentration in the field is accomplished by collecting the target compounds on a filter, adsorbent tube, or other collection media. Alternatively whole air samples can be collected in bags or canisters and then concentrated at the laboratory on sorbents or by cryogenic methods. Compound concentration in the field on adsorbent tubes was selected as the primary method for the prototype air monitoring station. Sampling was conducted using commercially available multi-bed adsorbent tubes tested with a wide range of compounds including the TO1, TO2, and TO3 compounds<sup>1</sup>. The adsorbent beds contained graphitized carbon black and carbon-molecular sieves. These adsorbents tubes trap compounds without regard to functional group using the principle of size exclusion. In addition, the adsorbents have a hydrophobic nature that is expected to reduce loss to water molecules. Advantages of this methodology include the following:

- direct exposure of the sampling media to the ambient air, without a sample line;
- the collection of greater air volumes for analysis (22 to 86 liters) than permitted by laboratory cryogenic methods (usually <1 liter); and
- the use of a mass spectrometric detection system for compound identification.

Prior to sampling, the adsorbent tubes are precleaned by heating to 330°C and purging with an ultra-pure helium flow of 9 cm<sup>3</sup>/min for 15 minutes.

The Wisconsin monitoring program does have experience with using canisters collection for photochemically reactive ozone precursors. The present analytical system for canisters is dedicated to the analysis of ozone precursors and lacks either multi-detector or mass spectrometer detection capabilities.

Sampler design. The sampler design is based on the TO1 design<sup>2</sup>, and the sampler used in the original USEPA Toxic Air Monitoring Station (TAMS) network<sup>3</sup>. The sampler consists of 4 major parts, a sampling manifold, flow controlling devices, an air mover, and an electronic timer. The sampling manifold has four independent channels each with a mass flow controller to monitor and regulate the air flow. A common timer and pump is used on the sample. All sampler parts are located inside an old high volume sampler housing. The four teflon vacuum lines extend out from the housing to a hood which shields the sampling tubes. Sampling tubes are inserted into the teflon lines and are directly exposed to the ambient air. A vacuum recorder provide a means of monitoring the sampling flow.

Sampling protocol. Twenty-four hour VOC samples were collected on a 1 in every 13 day schedule using a total of 5 sampling tubes. The primary samples (tubes 1 and 2) were simultaneously collected at flow rates of 15

cm<sup>3</sup>/min and 60 cm<sup>3</sup>/min. A duplicate set of sample tubes (tubes 3 and 4) were collected to insure a sample should an accidental loss occur to the first set. The fifth tube served as a field blank.

Unlike whole air sampling techniques (i.e. canisters) adsorbent sampling techniques are subject to complications such as background contamination, compound breakthrough, and artifact formation. Adsorbent sampling techniques must therefore use sampling schemes that will provide a definition of the sample quality. Such sampling schemes include the distributed volume technique (parallel sampling) and/or backup tubes (in series sampling). The distributed volume technique has been reported as a practical technique that is the preferred method of sampling for adsorbent tubes<sup>4</sup>. The sampling protocol adopted for this program requires adsorbent tube distributed volume sampling using 2 sampling tubes with air flows rates in a ratio of 1:4. The ambient concentration of each target compound collected is reported as the average of the two sample tubes with a Membership Value (MV) for the distributed volumes. Walling<sup>5</sup> has recommended the use of MVs determined by a one dimensional Gaussian function and evaluated by Fuzzy Set theory. Fuzzy Set theory assumes there is a continuous range of values reflecting the certainty in a measurement, rather than discrete values of certainty (good vs. not good). A MV of 1.0 indicates a perfect match between the two sampling tubes and a high degree of certainty in the result. As the MV decreases greater complication between the sampling tube pair is indicated, as is increased uncertainty in the results. For our data the Gaussian function is scaled to yield a MV of 0.92 for a 10% difference in the data pair. For the data reported in the Results Section a 25% difference for parallel tubes was used as one acceptance criteria. However this percentage can translate into different quantities at different levels. For example, at the 150 ppt a 25% difference is 38 ppt while this same percent difference at 25 ppt is only 6 ppt.

#### Analysis

The analytical system consists of an Envirochem Model 840 thermal desorption unit integrated with a Hewlett Packard 5995A gas chromatograph/mass spectrometer. Exposed sample tubes are thermally desorbed by ballistically heating from an ambient temperature to 270°C in 5 seconds; the tubes are held at 270°C while a 9 cm<sup>3</sup>/min helium sweep gas carries volatile compounds to a 2mm I.D. focusing tube. Focusing on the narrow I.D. minimizes dead volume and concentrates the columns needed into narrow bands, improving chromatography and eliminating the need for cryofocusing. The focus tube is spiked with the  $\alpha,\alpha,\alpha$ -trifluorotoluene internal standard used for quantitative analysis. The focusing tube is then thermally desorbed in the same manner onto the GC analytical column, a Suplecowax<sup>TM</sup> 10 glass capillary gas chromatographic column (60 meters x 0.75mm ID x 1.0  $\mu$ m DF). The sample is then subjected to a GC/MS analysis using a mass scanning mode ( 29 to 175 AMU).

The analytical method uses a 5 point standard calibration curve. The standards are prepared in a static bottle from a liquid stock solution of the target compounds. A headspace sample from the static bottle is then spiked onto a clean 4 mm Carbotrap<sup>TM</sup> 300 tube. Each analytical standard is desorbed and analyzed in the same manner as are the ambient samples. Daily operation of the analytical system includes the following: the GC/MS is autotuned using perfluorotributylamine; a blank with internal standards is run; a check standard is analyzed to verify calibration; a blind quality control sample is analyzed; and ambient samples are then analyzed.

During analysis of the first few sample sets, the analyst observed that some samples had components whose retention times were shifted during GC/MS analysis. Additionally, it was observed that the samples during the focusing step showed a white band which disappeared upon cooling. Water, picked up from the humid ambient air, was the suspected source of the chromatographic changes. Standards were prepared, spiked with various amounts of water and analyzed. Analysis of the spiked samples confirmed that the water did cause the retention time shift. Losses of xylene, cumene, n-butanol, and limonene were seen as well. A pre-analysis nitrogen purge was added to remove water from the ambient samples. Experiments were conducted to determine the best gas flow rate and total drying time required. We elected to dry with a nitrogen purge at 20 to 30 cm<sup>3</sup>/min for 4 hours.

## RESULTS AND DISCUSSION

#### Data Quality

Field blanks. Each complete sample consists of two sampling tubes and a blank. Because the sampling tubes aggressively scavenge compounds from the air, a field blank is needed to indicate possible contamination. As an example of scavenging ability, an August 1991 sample blank was contaminated when the transport tube broke in transit. Upon analysis the tube showed heavy concentration of all compounds ranging from >1000 ng for hexane to 100 ng for benzene. Examination of the blanks showed that acetone, hexane (used at the site), toluene and xylene

were the most commonly found contaminants in the field blanks. In calculating all results, the blank was subtracted prior to calculation of the ambient concentration.

**Replicate samples.** In theory, the use of the distributed volume sampling method, will require that every sampling set contains duplicate samples. In addition to distributed volumes, replicate samples with identical flow rates were periodically collected for analysis. These duplicates did show relative average differences ranging from 0% to 100%. A 100% difference denoted sample pairs where a compound was detected in only one tube. The highest variation was found in isopropanol and the lowest in benzene.

**Audit samples.** The USEPA supplied the Wisconsin program with two audit samples. These audit samples consisted of VOC sampling tubes that were spiked with known concentrations of selected compounds. Analysis of these samples showed the expected loss of the compounds from the more volatile compounds. Preliminary data from laboratory standards and USEPA audits does however suggest poor recovery of the most volatile compounds (1,3-butadiene and acetone). Suggesting that the preanalysis nitrogen purge causes loss of these compounds. The remaining compounds showed better result. Six of 16 compound data points did exceed the 25 % accuracy goal in the draft Quality Assurance Project Plan.

### Monitoring Results

The compiled results of the VOC monitoring from November 1991 to November 1992 are summarized in Table 1. Analytical results from the two sample tubes, with distributed volumes, were averaged and the data from the 28 sample sets were evaluated against the following 3 criteria:

- was the compound detected in the sample;
- was the compound detected at concentrations greater than the minimum quantitation limit (MQL); and
- was the MV for the tube pair greater than 0.673 (equivalent to a percent difference of 25%).

Each one of 28 sample sets was analyzed for 20 compounds resulting in a possible 560 data points. The results are broken down in the following manner:

- 41.6 percent of the time compounds were not detected;
- 22.9 percent of the time detected compounds were less than MQL;
- 22.3 percent of the time the MV indicated a unacceptable difference in results from the sample pair; and
- 13.2 percent of the results were detectable and quantifiable.

Table 1 reports the number of detects and the range of the quantifiable results. There was insufficient data to calculate an accurate annual ambient mean for most of the compounds monitored. The VOC monitoring data is consistent with other studies<sup>6,7,8</sup> that have found benzene, toluene, and xylene to be among the most commonly found compounds. Perchloroethylene was the most commonly detected chlorinated compound with detects in 25 of 28 samples. However, only 7 samples had data that meet acceptance criteria for quantitation. Concentrations at the Bay Beach site have been generally lower than the mean values reported for National Urban Air Toxics Monitoring Program (UATMP). Comparison of the 1989 and 1990 median concentrations for the UATMP with median concentration reported in Table 1 show the following: the benzene concentration was 24-33% of the median UATMP concentrations; the toluene concentration was 21-27% of the median UATMP concentrations; the xylene concentration was 18-35% of the median UATMP concentrations; and the perchloroethylene concentration was 31-48% of the median UATMP concentrations.

Careful examination of the remaining monitoring data can provide clues about the ambient concentrations of other pollutants. Dichlorobenzene is a compound found in extremely low ambient concentrations and the monitoring results of this compound offer a good example of the additional ambient information monitoring provides. Twelve of twenty eight samples for dichlorobenzene were reported out as no detects, while 12 were listed as below MQL. In the latter 12 cases only one of the tube pair was below the MQL. However, because 1 of the pair was below the MQL, the MV test (the next criteria) could not be applied. If the MV test were applied 3 of the 12 pairs would showed excellent agreement (MV 0.899 or better) and would represent concentrations of 0.016, 0.015, and 0.029 ppb. The remaining four BAD PAIR cases reported for dichlorobenzene were monitored at low concentration and despite percent differences greater than 25% for 2 samples (0.049 ppb and 0.032 ppb) this amounted to only 13 ppb in the pair results. Overall we conclude dichlorobenzene was present in the ambient air and in concentrations of less than 50 ppt. Efforts to improve detection of the dichlorobenzene should focus on collection of greater air volumes.

The Bay Beach Monitoring location was chosen because of the predominant southerly wind in the Green Bay area. Daily vector means of the wind direction data, collected at the site, have shown that the wind direction on 82%

of the sampling days falls between 90° and 270°; on 50% of the sampling days the winds were from a sector of 180° to 270°. All VOC sources are to the south of the site and as expected, the highest concentrations of compounds were also found in winds from the southwest quadrant (see Figure 1). Among the original plans for the data was the use of multi-variant statistical techniques (principle component analysis and factor analysis) to determine the source of measured compounds. However, with a large percentage of the data being none detected or below the MQL these statistical techniques can not be used with confidence. At this time, no attempt has been made to correlate any of the monitoring data with specific sources in the area or with the WDNR's developing Air Toxics Emissions Inventory.

## CONCLUSIONS

Monitoring at the Bay Beach site has met the goals of collecting preliminary data on concentrations of air toxics in the urban environment. Monitoring has provided concentration estimates for target compounds such as benzene, toluene, and xylene. In addition, monitoring has provided information on the level of sensitivity that will be needed to monitor target compounds such as dichlorobenzene. Finally we see that the preanalysis nitrogen purge, required to dry the adsorbent sampling tubes causes loss of the most volatile compounds, such as 1,3 butadiene. An alternative method, such as whole air sampling, will be required to monitor this and other highly volatile compounds.

The large number of non detects may be due to the relative remoteness of the Bay Beach site from the central business district with its many area sources. The demonstration of successful urban monitoring at the Bay Beach station has facilitated a site move to a new station site located within the city's central business district. While we will continue to use the adsorbent tube for sampling at the new station, we are in the planning stages of a change to a whole air sampling scheme using canisters. We believe that whole air canister sampling will be a better choice for an urban air toxics network for the following reasons:

1. canister sampling simplifies the sample collection and sampling handling;
2. canister sampling will transfers many sample quality concerns from the field to the laboratory; and
3. the sampling method will be consistent with National Urban Air Toxic Monitoring Programs.

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TABLE 1: Summary statistics for VOC concentrations (ppb) monitored in Green Bay

NAME	MEAN	MEDIAN	MIN	MAX	DETECT	NON-DETECT	<MQL	BAD PAIR
1,3-Butadiene					0	28	0	0
2-butanone (MEK)		0.111	0.111	0.111	1	16	7	4
acetone		0.349	0.349	0.349	1	8	7	12
alpha-pinene					0	19	7	2
benzene	0.348	0.332	0.080	1.145	18	0	1	9
chloroform					0	19	8	1
cumene	0.020	0.018	0.018	0.024	3	12	8	5
ethanol					0	18	7	3
isopropanol		0.184	0.184	0.184	1	17	7	3
limonene					0	20	4	4
methyl chloroform	0.190	0.190	0.176	0.204	2	0	8	18
methylene chloride		0.127	0.127	0.127	1	13	12	2
n-butanol	0.213	0.213	0.149	0.277	2	13	11	2
n-hexane	0.784	0.771	0.353	1.393	5	2	7	14
p-dichlorobenzene					0	12	12	4
stryrene					0	15	9	4
perchloroethylene	0.096	0.096	0.038	0.197	7	3	8	10
toluene	0.628	0.519	0.035	1.829	14	0	0	14
trichloroethylene	0.025	0.024	0.018	0.033	3	18	5	2
xylene	0.522	0.351	0.021	1.736	16	0	0	12
Totals					74	233	128	125
					13.2%	41.6%	22.9%	22.3%

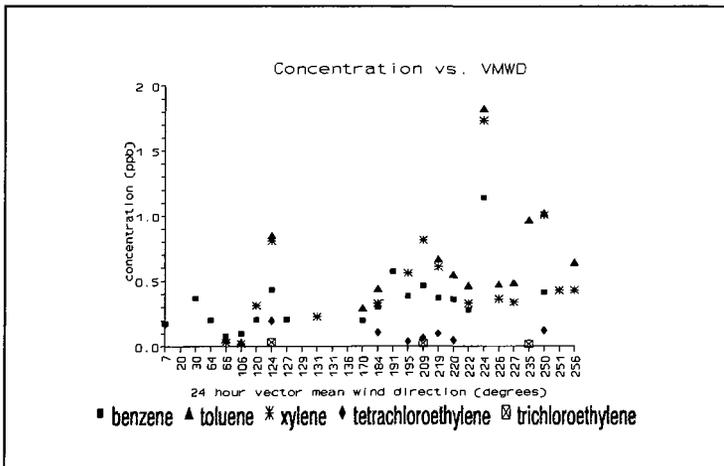


FIGURE 1: Selected compound concentrations plotted against the sampling day vector mean wind direction.

## COMPARISON OF NMOC DATA COLLECTED BY TWO METHODS IN ATLANTA

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### ABSTRACT

The Clean Air Act Amendments of 1990, Title I, call for "enhanced monitoring" of ozone, which is planned to include measurements of atmospheric non-methane organic compounds (NMOC's). NMOC concentration data gathered by two methods in Atlanta, Georgia during July and August 1990 are compared in order to assess the reliability of such measurements in an operational setting. During that period, automated gas chromatography (GC) systems (FIELD systems) were used to collect NMOC continuously as one-hour averages. In addition, canister samples of ambient air were collected on an intermittent schedule for quality control purposes and analyzed by laboratory GC (the LAB system). Data from the six-site network included concentrations of nitrogen oxides ( $\text{NO}_x$ ), carbon monoxide (CO), ozone, total NMOC (TNMOC), and 47 identified NMOC's. Regression analysis indicates that the average TNMOC concentration from the LAB system is about 50 percent higher than that from the FIELD system, and that the bulk of the difference is due to unidentified NMOC's recorded by the LAB system. Also, there are substantial uncertainties in predicting a single FIELD TNMOC concentration from a measured LAB concentration. For individual identified NMOC's, agreement is poor for many olefins that occur at low concentrations but may be photochemically important. Regressions of TNMOC against CO and  $\text{NO}_x$  lead to the conclusion that the larger unidentified component being reported by the LAB system is not closely related to local combustion or automotive sources.

### DISCLAIMER

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

## INTRODUCTION

In July and August of 1990, the Atmospheric Research and Exposure Assessment Laboratory (AREAL) conducted a field study in Atlanta, Georgia to obtain data on atmospheric pollutants related to ozone formation in the urban area. Six sites were established in the Atlanta area where nonmethane organic compounds (NMOC's) were measured continuously by an automated gas chromatograph on an hourly basis<sup>1</sup>, as were meteorological data and other pollutants, e.g. carbon monoxide, ozone, nitrogen oxides. In addition to the continuous data, air samples were collected in stainless steel canisters and analyzed later for NMOC's by a laboratory gas chromatograph.<sup>2</sup> This paper focuses on a comparison between the NMOC measurements taken by the two methods.

The Atlanta Ozone Precursor Study was conceived, in part, as a prototypical demonstration for "enhanced monitoring" related to ozone as called for in the Clean Air Act Amendments of 1990. A complete description of the measurements taken during the study can be found in the Data Report.<sup>3</sup> A second report<sup>4</sup> supplements the Data Report by giving some alternative perspectives and more in-depth presentations of the data from the continuously operated sites, including diurnal curves of all major pollutants.

## NMOC MEASUREMENTS

An automated gas chromatographic (GC) system (Chrompack, Inc.), hereinafter designated the FIELD system, was used to measure NMOC's each hour and at each of the six sites. A sample was collected in an absorbent trap for 30 minutes and then analyzed in the following 30 minutes. The FIELD systems were in place from July 1 through August 31, 1990, giving 1488 possible hourly measurements. The final FIELD archive holds, for the various sites, NMOC concentration values for 50-70 percent of the possible hours.

Air samples were collected in stainless steel canisters at Sites 1-6 on a schedule of approximately every other day and at times that rotated through the diurnal cycle. The canisters were opened for the first 30 minutes of the hour and so collected a sample comparable to that taken by the collocated FIELD system. The canisters were returned to AREAL at Research Triangle Park, NC, within a few days and NMOC's were measured using a laboratory HP 5890 GC. A total of 174 samples were collected, analyzed, and archived. Hereinafter, this collection and analysis method will be referred to as the LAB system.

The archive of the FIELD data contains 47 identified NMOC's as well as TNMOC, the sum of all identified and unidentified NMOC's (ppbc). The archive of the LAB data contains comparable NMOC's.

## COMPARISON OF FIELD AND LAB MEASUREMENTS

There are a total of 174 hourly LAB measurements available. However, the FIELD system reported measurements at only 85 of these times and sites. Because the FIELD system, at some sites and times, reported erroneously high values of isopentane, and because of evidence that the problem extended to other NMOC's, 21 measurements had to be deleted. In addition, there were several "outliers." After these deletions, 58 measurements remained to be compared from the two systems.

Figure 1 gives the regression line (FIELD vs LAB TNMOC) for the remaining measurements and includes the 90 percent prediction interval. The slope of the regression line is 0.64 with a standard error of 0.05. The prediction interval gives a sense of the ability to predict an individual FIELD measurement from a LAB measurement. If, for example, there is a single LAB measurement of 400 ppbC TNMOC, the FIELD system would be expected to return a value between 130 and 380 ppbC nine out of ten times. Obviously the disagreement between single measurements is considerable.

Simple linear regressions, similar to that shown in Figure 1, were repeated for the sums of all identified NMOC's and the sums of all unidentified NMOC's. The regression lines and prediction intervals are given in Figures 2 and 3, respectively. For the identified NMOC's, the estimated slope is 0.896 with a standard error of 0.04 and a non-significant intercept of 2.5 ppbC, showing that the LAB system tends to report a value only about 11 percent higher than the FIELD system. For the unidentified NMOC's, the slope is 0.16 with a standard error of 0.05 and a non-significant intercept of 32 ppbC. Clearly the major problem lies with the unidentified NMOC's.

Simple linear regressions were also performed for each of the 47 identified NMOC's, and the results for slope and  $R^2$  indicate that many individual NMOC's do not compare well. Of the 12 NMOC's having  $R^2$  below 0.50, all but two have average concentrations much less than 1 percent of TNMOC, so the poor explanation of variability may be due to insufficient instrument sensitivity.

Mobile sources are a principal contributor to NMOC in Atlanta and other U.S. cities, and therefore one would expect a relation between TNMOC and other combustion related gases, carbon monoxide (CO) and nitrogen oxides ( $\text{NO}_x$ ). Figure 4 gives a linear regression and 90% prediction interval for TNMOC from both systems against CO. Regressions with similar features are found for TNMOC vs  $\text{NO}_x$ . The Figures reveal a much greater unexplained variability in the LAB TNMOC as measured by the root mean square error (rmse). Similar regressions were computed using the sums of identified and unidentified NMOC's. Considering the identified components, regressions for the two systems were quite close in all aspects. The differences in slope, intercept, and rmse seen in Figure 4

arise almost entirely from the unidentified components of the two systems. One concludes that the (larger) unidentified component that is reported by the LAB system is not closely related to local automotive or high-temperature combustion sources.

#### **CONCLUDING REMARKS**

The 1990 Atlanta Study provides an interesting glimpse at the problems that may be encountered in implementing routine measurements of NMOC's in urban areas, where somewhat different instruments and procedures may be used. The Atlanta study was not designed as an instrument comparison, with rigorous controls and side-by-side processing, and in that respect probably more realistically simulates the type of outcome that may occur in operational networks. On the other hand, the Atlanta data were taken over only a two month period, and start-up problems with emerging auto-GC technology could be addressed in a longer time period.

There are large differences between the NMOC concentrations reported by the two GC systems in the Atlanta study, even given rather careful data editing. The results demonstrate that reliable NMOC measurements are difficult to obtain and show the necessity for a strong quality control component in the "enhanced monitoring" program. This paper presents statistical and graphical techniques that will be useful in future quality control analyses.

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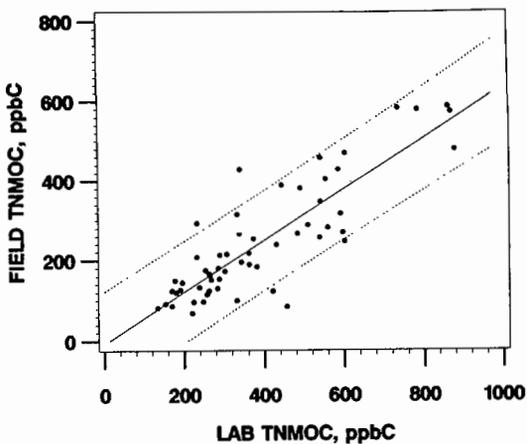


Fig 1. Linear regression of FIELD TNMOC against LAB TNMOC, including a 90 percent prediction interval.

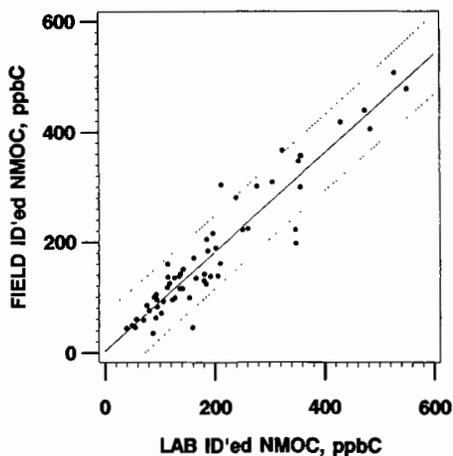


Fig 2. Linear regression of FIELD identified NMOC against LAB identified NMOC, including 90 percent prediction interval.

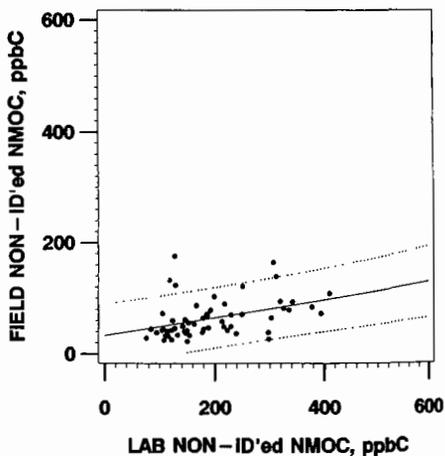


Fig 3. Linear regression of FIELD unidentified NMOC against LAB unidentified NMOC, including 90 percent prediction interval.

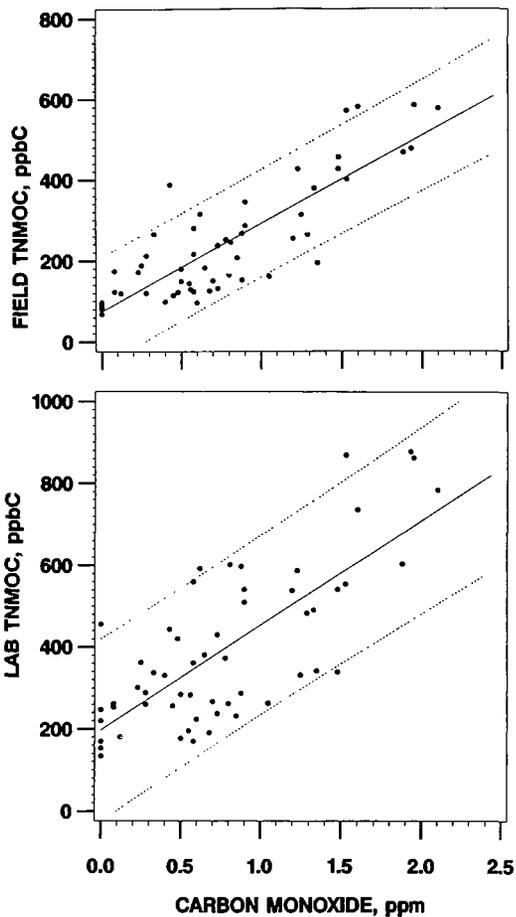


Figure 4. Linear regressions of FIELD and LAB TNMOC's against carbon monoxide, including a 90 percent prediction interval.

## VOCs in Mexico City Ambient Air

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### ABSTRACT

Mexico City, with nearly 20 million people, 3 million vehicles, and 35,000 industrial businesses, has severe photochemical air pollution.<sup>1</sup> The Mexican O<sub>3</sub> standard of 0.11 ppm is exceeded over 300 days of the year. Because of the role of VOCs in the production of O<sub>3</sub>, a study of the concentration and composition of VOCs in ambient air was undertaken. From March 6 to 26, 1992, 68 ambient air samples were collected on week-days in passivated stainless steel spheres at four sites in Mexico City. Most (52) sampling was in the morning from 6:00-9:00 am, however at 2 sites 18, 12:00-3:00 pm afternoon samples were collected. Ten morning samples were also taken at two background sites north of the city. The samples were analyzed by capillary gas chromatography-flame ionization detection (gc-fid) for C-2 to C-14 hydrocarbons. CO and CH<sub>4</sub> were also determined. Total non-methane organic compound (TNMOC) concentrations were very high. In the 6-9 am period TNMOC ranged from 1.49 to 6.94 ppm. The afternoon results were lower, ranging from 0.48 to 3.06 ppm. TNMOC at the two background sites ranged from 0.16 to 1.64 ppm.

### INTRODUCTION

Mexico City is within a mountain basin at an elevation of 2234 m, surrounded by peaks 3500 m average height with some peaks reaching over 5000 m. Almost 20 million people, close to 3 million vehicles and a significant portion of the nation's industrial base lie within the Mexico City Metropolitan Area (MCMA) basin. Because of its rapid growth, 35,000 industries of all sizes and types are spread over the city with slightly higher concentration in the north and east. The subtropical climate combines with the geographic characteristics to intensify and concentrate air pollutants from industrial, transportation, and routine daily activities. The basin is relatively small, 120 x 150 km, however population activities are concentrated in an even smaller area, 2346 km<sup>2</sup>, at the middle of the basin. High solar radiation at the high altitude and strong inversions provide conditions for the production of photochemical pollution. The Mexican O<sub>3</sub> standard, of 0.110 ppm, was exceeded more than 300 days in 1991.<sup>1</sup>

A 25 station network monitors O<sub>3</sub>, SO<sub>2</sub>, NO<sub>2</sub>, NO<sub>x</sub>, CO and meteorological parameters throughout the MCMA. However, hydrocarbons are measured at only 3 stations by means of analyzers with photoionization detectors that have highly variable individual hydrocarbon responses.

quantitation individual species not detailed enough to be used for the evaluation of hydrocarbon impact on O<sub>3</sub> formation. A field study was conducted in March 1992 to determine C-2 to C-14 ambient total and speciated hydrocarbon concentrations at 4 sites within and 2 sites upwind of the MCMA. CO and CH<sub>4</sub> measurements were also made. This paper presents the results of that field study.

## EXPERIMENTAL METHODS

Six sites were selected for sampling. Three sites were monitoring stations at Xalostoc, Merced, and Pedregal which lie on a northeast to southwest line through the center of the city. This line corresponds to the most frequent wind trajectory. Xalostoc is an industrial area, Merced is a commercial area characterized by heavy traffic, and Pedregal is residential area where the city's highest O<sub>3</sub> concentrations are normally recorded. The station at Tlalnepantla, an industrial/commercial area to the northeast, was also selected, because the highest O<sub>3</sub> readings are sometimes observed there. All of these 4 sites contained a full compliment of pollutant monitors. The two upwind sites were at Cuautitlan which is a university campus due north of the city and east of a major north/south highway and La Reforma which is northwest of Cuautitlan near the small town of La Reforma.

Ambient air samples were collected on weekdays from March 6 to 26, 1992. Microprocessor controlled samplers pumped air into passivated stainless steel spheres. Fifty-two samples were collected from 06:00 to 09:00 at the Xalostoc, Tlalnepantla, Merced, and Pedregal monitoring stations. At Tlalnepantla and Pedregal 18 midday (12:00-15:00) samples were also taken. Two upwind sites north of the city, Cuautitlan and La Reforma, were used to collect 5, 06:00-09:00 samples each.

The samples were analyzed at EPA, Research Triangle Park by gas chromatography with flame ionization detection (GC-FID) using 3 different columns. C-2 to C-14 hydrocarbons were separated on a 60-m, 0.32 mm i.d. fused silica capillary column with a 1 μm thick film of a non-polar cross-linked liquid phase (DB-1, J&W Scientific, Rancho Cordova, CA). Ethylene, acetylene, and ethane were separated on a 30-m, 0.53 mm i.d. GS-Q porous polymer open-tubular fused silica column (J&W Scientific), because they were not consistently resolved on the 60-m non-polar column. The C-2 to C-14 hydrocarbons were cryogenically preconcentrated in a 11" x 1/8" o.d. U-shaped trap filled with 60-80 mesh glass beads cooled by liquid argon in a Dewar flask. Injection was accomplished by switching a 6-port gas sampling valve and heating the trap with near boiling water. In the case of the C-2 hydrocarbons the trap was filled with Carbowax 20 M on 60-80 mesh Chromosorb W-AW and heated by room temperature water. The details of these analyses are published elsewhere.<sup>2</sup> CH<sub>4</sub> and CO were resolved on a 2-m x 1/8 in od ss column containing 40-60 mesh molecular sieve. CO was catalytically reduced to CH<sub>4</sub> by H<sub>2</sub> on a nickel catalyst at 350°C for detection by FID.

## RESULTS AND DISCUSSION

Figure 1 is a box and whisker plot showing the total non-methane organic compound (TNMOC) results for each site and time period of the study. TNMOC was calculated by summing all of the individual peak concentrations from the DB1 column except for ethane, ethylene, and acetylene whose concentrations came from the GS-Q analysis. The center vertical line of a box is the median. The hinges represent the 25th and 75th percentile values. The inner and outer fences

are defined as  $\pm 1.5$  and  $\pm 3.0$  times interquartile range from each hinge. The whiskers show the range of values which fall between the inner fences. Values outside the inner fences are plotted with asterisks, and values outside the outer fences are plotted with empty circles.

The highest median (4.44 ppm) corresponds to Xalostoc which is mainly an industrial area, although we do not mean to imply an absence or even much diminution of automobile traffic, because there is significant automobile traffic everywhere in Mexico City. Additionally, at this station the concentration dispersion is the largest, ranging from 1.93 to 6.94 ppm. The downtown station, Merced, which is in an area influenced by combined commercial and vehicular activities, recorded the second highest median (3.50 ppm) with correspondingly lower dispersion, 4.29 ppm. The urban site of lowest morning median TNMOC reading was Pedregal (1.98 ppm) which is in primarily a residential area.

The difference in concentration between morning and midday samples is higher at the northwestern site of Tlalnepantla (1.785 ppm or 55% reduction from morning samples) than at Pedregal. The lesser midday reduction, 0.443 ppm (22%), at the SW station may be attributed to the prevailing atmospheric transport, NE to SW, from the central urban area in addition to local emissions. This fact in addition to Pedregal being the site showing the highest frequency of maximum ozone readings point to it at an important receptor site.

A comparison of the Mexico City TNMOC results to levels in US cities is also shown in Figure 1. The US statistics are from a continuing study of 6 to 9 am TNMOC and NO<sub>x</sub> concentrations at urban sites in cities that have not met the ambient air quality standard for O<sub>3</sub>. Integrated ambient air samples were collected during the late spring and summer months in passivated 6-l stainless steel spheres and air freighted to a central laboratory for analysis by the cryogenic preconcentration direct flame ionization (PDFID) method. Over 10,000 samples from 68 cities were analyzed over a 6 year period. The US boxes in Figure 1 were constructed from the statistical results rather than from all of the individual measurements.<sup>3,4,5,6,7</sup> Therefore values less than the inner or greater than the outer fences are not shown with the exception of the maximum values. Although US TNMOC maximums are very high, it is clear that TNMOC in Mexico City is significantly higher than TNMOC in the US; in terms of medians from 2 to 8 times higher. This holds true even at the two midday sampling sites as well as the two morning upwind sites.

The two upwind sites' TNMOC was much lower than that of the urban sites although well above U.S. urban 6-9 am TNMOC. These high measurements at the outlying sites are at least in part due to local emissions from nearby sources. The Cuautitlan site was about 200 m from a major highway, although the highway was not upwind of the prevailing wind direction. The La Reforma site was near a small town. These measurements are probably an over estimate of the true boundary conditions.

The most abundant hydrocarbon species are listed in Table 1. The data in this table are morning results from the 4 MCMA sites: Tlalnepantla, Xalostoc, Merced, and Pedregal. The mean concentrations are averages of the morning site medians, thus they are not influenced by the number of samples taken at each site. Each site has equal influence. The maximum concentration represents the overall maximum for all 6 sites, because no maximums were observed in the afternoon samples or at the boundary sites. All maximums were observed in the morning at Xalostoc with the exception of isopentane, benzene, and MTBE (methyl-t-butylether) at Merced. Compound ratios to TNMOC expressed as percentages are shown in the "composition" column of

the table.

The table consists of 7 paraffins, 3 aromatics, an olefin, acetylene, and MTBE. These 13 compounds account for a little more than 50% of the TNMOC. The most abundant hydrocarbon was propane which is used as a household cooking and commercial fuel. Propane maximum concentration and highest median, 617 ppbC, were observed at Xalostoc. Although Pedregal had the lowest propane morning median concentration, 313 ppbC, it nevertheless had the highest morning mean propane composition, 17.7%. The other compounds in Table 1 are associated with vehicular related sources including exhaust and evaporation of gasoline. The gasoline additive, MTBE, was observed in all samples except two at La Reforma. The maximum concentration, 122 ppbC and highest median, 65 ppbC, were recorded at Merced, the site in the area of highest traffic flow.

## CONCLUSIONS

Mexico City TNMOC was very high, on average from 3 to 8 times that of U.S. cities for the 6 to 9 am time period. In addition TNMOC at the background sites was also high compared to U.S. cities. Propane was the most abundant hydrocarbon followed by paraffins and aromatics associated with automobile exhaust and gasoline evaporation. MTBE was prominent: it was present in all but two background samples and was the twelfth most abundant compound in the MCMA morning samples.

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Table 1. Most abundant hydrocarbons in Mexico City ambient air.

Compound	Mean Conc. ppbC	Maximum Conc. ppbC	Composition % of TNMOC
Propane	463	852	12.9%
n-Butane	286	613	8.6%
Toluene	170	446	5.2%
i-Pentane	140	309	3.8%
i-Butane	133	281	4.0%
n-Pentane	128	304	3.8%
Acetylene	111	263	2.5%
Ethylene	94	226	2.9%
m & p-Xylene	77	202	2.3%
2-Methylpentane	69	170	2.3%
n-Hexane	66	198	1.8%
MTBE	47	122	1.3%
Benzene	45	100	1.4%

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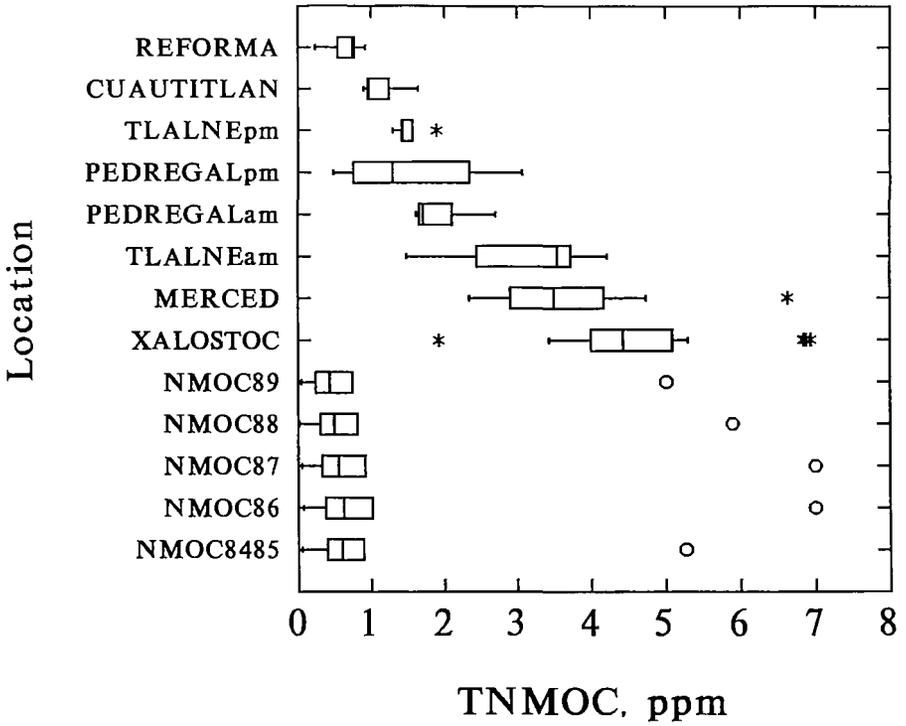


Figure 1. Mexico City TNMOC

**MONITORING STUDIES OF AMBIENT LEVEL VOCs and CARBONYLS  
in PHOENIX, ARIZONA**

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**1. INTRODUCTION and OBJECTIVES**

The Phoenix metropolitan area has been classified by the U.S. Environmental Protection Agency (EPA) as a "moderate" nonattainment area for Ozone (O<sub>3</sub>). The 1990 Clean Air Act Amendments require states to submit complete O<sub>3</sub> State Implementation Plans (SIP's) by November 1993. With these objectives in mind, ADEQ prepared a document entitled Workplan For Development of The Phoenix Ozone SIP, March 1992. This workplan called for a modeling analysis to define the relationships between emissions of precursors and the formation of ozone. The most appropriate model for this purpose is the Urban Airshed Model (UAM) which requires an extensive air quality, meteorological and emission database. Part of this required database is available from air quality and meteorological networks routinely operated by various governmental and industrial organizations. However, certain elements of the required database are not routinely monitored and they include:

- Upper level meteorological and air quality data
- VOC, Carbonyl and NO<sub>x</sub> air quality data
- Background air quality data

Consequently, ADEQ found it necessary to conduct a monitoring study to collect these unavailable data elements. Thus, the basic study objectives can be summarized as follows:

- Collect meteorological and air quality data required to support a UAM analysis for the Phoenix airshed.
- Collect quality monitoring data for VOCs and carbonyls to be used in the Phoenix O<sub>3</sub> modeling analysis.

**2. SAMPLING NETWORK**

The VOC/Carbonyl sampling network consisted of a total of six monitoring sites summarized in Table 1. Three sampling periods, 6 am to 8 am, 10 am to 12 pm, and 3 pm to 5 pm, are scheduled per each sampling day. The VOC sampling period started from August 10, 1992 to October 30, 1992. In some cases, the sampling was

cancelled if ozone did not promisingly approach the violation limit, 120 ppb. Non-methane organic compounds (NMOC) were continuously monitored at supersite from Oct. 11 to October 30, 1992.

The carbonyl sampling started from Aug. 26, 1992 for all sites except Volkswagen Proving Ground, which started by Sept. 9, 1992. The sampling activities stopped by Oct. 7, 1992.

Table 1

Location Code	Site Name
1	South Scottsdale
2	Supersite
3	Valley National Center
4	Chandler Heights
5	Central Phoenix
6	Volkswagen Proving Ground

### 3. LABORATORY ANALYSIS

#### VOC Samples:

The VOC sample analyses from SUMMA canisters were performed by ENSR Consulting and Engineering complying with the EPA method TO-14. The samples were cryogenically preconcentrated and then analyzed by a GC-FID-ECD-PID system. The target species for the analysis are listed as follows.

Acetylene	1,1,1-Trichloroethane
Propylene	Trichloroethylene
Propane	Tetrachloroethylene
Butane	Benzene
Pentane	Toluene
Hexane	Chlorobenzene
Octane	Ethylbenzene
Isoprene	m-Xylene
Methylene Chloride	o-Xylene
1,1-Dichloroethylene	p-Xylene
Chloroform	Styrene

#### Carbonyl Samples:

The analyses of C-18 DNPH cartridges for carbonyls were performed by ENSR Consulting and Engineering pertaining to the requirements of EPA method TO-5. The target species for the analysis are listed

as follows:

Formaldehyde  
Acetaldehyde  
Acrolein  
Methylethylketone  
Acetone

Carbonyl in the ambient air reacted with DNPH to form stable hydrazone derivatives, which are separated and quantified using HPLC equipped with a UV detector at 360 nm. The quantities of hydrazones detected were used to determine the quantities of carbonyl by comparing with external standards.

#### 4. RESULTS

Figure 1 and Figure 2 summarize the average NMOCs, BETX, and carbonyl readings. Acrolein was not detected at any site.

Chandler Heights, a suburban location at south-east valley, and Volkswagen Proving Ground, a suburban location at west valley area, appeared to be good background sites, whereas other sites represent areas affected by urban pollution sources.

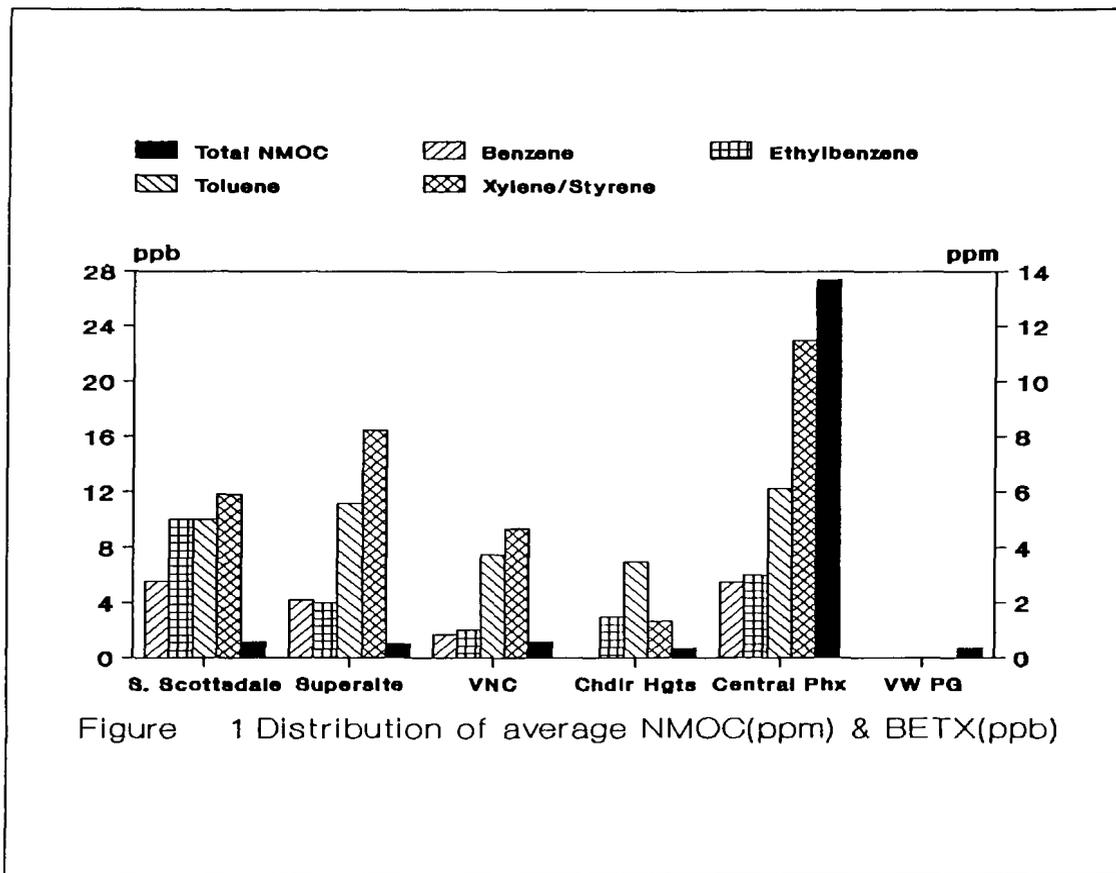
South Scottsdale at an east Phoenix metropolitan area has appreciable amount of nearby automobile traffic. The average NMOC is 580 ppb, about 57% more than that at Chandler Heights.

Supersite is located at a central Phoenix residential area. The average NMOC is 538 ppb, about 45% higher than the average at Chandler Heights.

Valley National Center at a central Phoenix area collects samples from a higher elevation than other sites. The NMOC concentration is 604.5 ppb, about 63% more than that at Chandler Heights. But the overall readings at Valley National Center are slightly lower than those at other urban locations.

Central Phoenix site is at downtown Phoenix where heavy bus and car traffic is within 300 feet of distance. There is a parking lot within 50 feet to this site. The concentrations of most non-chlorinated VOCs are significantly higher than those of other sites. The average NMOC is nearly 14 ppm as compared to a few hundred ppb at other sites. Central Phoenix also has the highest average carbonyl concentrations of all sites.

Figure 3 shows NMOC concentrations detected at the monitoring sites during the sampling period of Aug. 10 to Oct. 30, 1992. Concentrations detected at Central Phoenix were in the ppm range, using the right-hand Y-axis. Concentrations from other locations are mostly in ppb range, using the left-hand Y-axis.



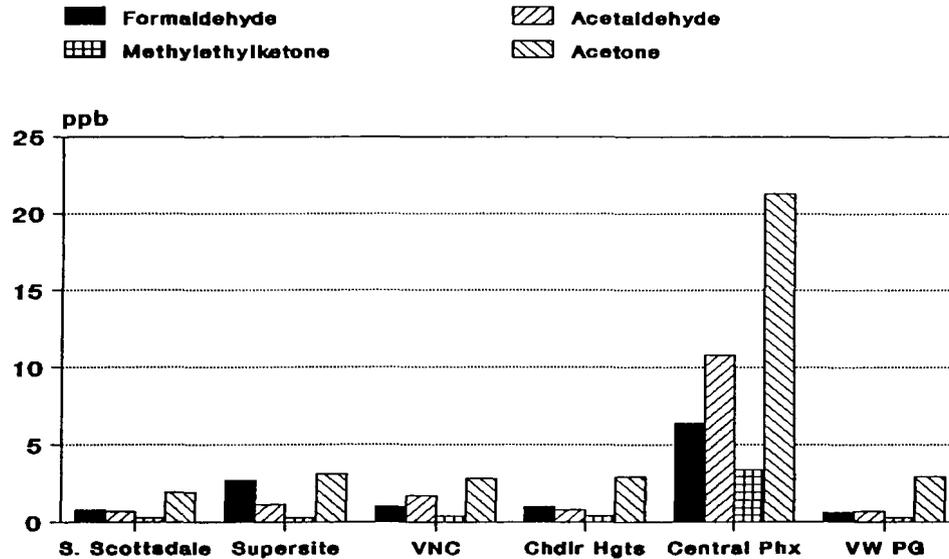


Figure 2 Spatial distributions of average carbonyl(ppb)

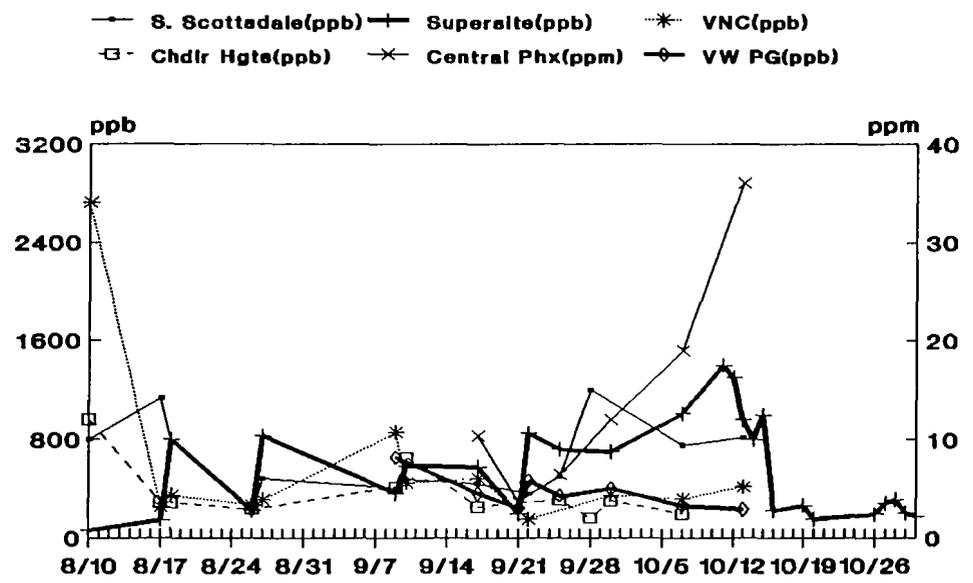


Figure 3 Average daily NMOC at the six monitoring sites

## AN AUTOMATED SYSTEM FOR THE ON-LINE ANALYSIS OF OZONE PRECURSORS

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### 1. ABSTRACT

A Perkin-Elmer Model ATD-400 Thermal Desorption System was specially adapted for the collection of whole-air samples. The  $C_2$  to  $n-C_{10}$  hydrocarbons were trapped using Peltier cooling on Carbotrap®/Carbosieve® adsorbents at  $-30^\circ C$ . Multidimensional chromatography allowed the  $C_2$  to  $C_6$  compounds to be separated using a porous layer open tubular column while a methyl silicone column separated the  $C_6$  to  $C_{10}$  fraction. No cryogen was used in the collection or analysis. An air generator equipped for automatic restart and special software allowed the system to recover from power failures. Ozone precursor concentrations were detected over 5000 hours of continuous operation at the 0.1 ppbV level. Area repeatability was below 10%, with retention time precision over 100 hours of approximately 1% RSD for most compounds. Remote communications allowed chromatography to be monitored and files to be downloaded to a central office at 19.2kbaud. Data in .CSV format was directly assimilated by spreadsheet software for graphing and customized reporting. Data were archived using external Bernoulli® disks.

### 2. INTRODUCTION

The 1990 Clean Air Act Amendments require that ambient air be monitored for certain VOCs which catalyze the formation of ozone in the presence of oxides of nitrogen and sunlight [1,2]. A system has been designed [3] that allows these VOC species to be sampled from the ambient air on a regular basis to provide a continuous record.

It would be preferable if such a system be capable of running for long periods of time unattended, since, for most of these sampling sites, no permanent operator is located and relative inaccessibility would make the guaranteed supply of replacement consumables such as liquid cryogen next to impossible. The design of a system required for such an installation must therefore provide for a high degree of robustness and automation. Following field trials it was seen that the system must be able to survive a power outage and bring itself back on line automatically.

This paper describes some ideas and concerns leading to the implementation of such a system, and some experiences and findings following (in excess of) 5000 hours of continuous operation on one such system.

### 3. INSTRUMENT DESIGN

A schematic of the system is shown in Figure 1. A 600mL sample of air (typically, but not limited to, ambient air) is drawn by means of a small sampling pump through the cold trap of an ATD-400 thermal desorber.

The trap lower temperature is set to  $-30^\circ C$  by peltier effect (electric) cooling while the air sample is obtained. The design of this trap has been previously described [4]. Once the sample is collected the trap is heated at  $2400 degC/min.$  to  $325^\circ C$  to ensure that the VOCs are desorbed rapidly from the cold trap in a fast,

focused band consistent with the requirements of the capillary column. (Figure 2). During this process the desorbed gas flow through the trap is reversed to prevent the more volatile components from contacting the stronger adsorbent.

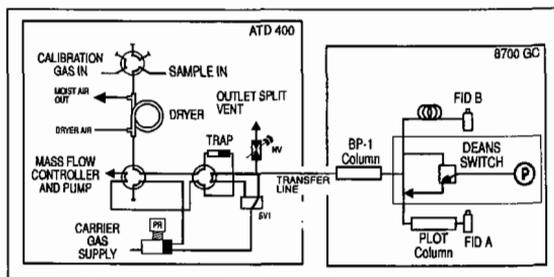


Figure 1. Sample Collection

#### 4. SAMPLE ANALYSIS

The first GC column is a 50m x 0.22mm ID x 1.0µm methyl silicone (BP-1®). The first (approx. 12 minutes) of compounds eluting from the BP-1 are switched by a pressure-balanced Deans' switch[5] to a 50m x 0.32mm ID Al<sub>2</sub>O<sub>3</sub>-Na<sub>2</sub>SO<sub>4</sub> porous layer open tubular (PLOT®) column and detected by an FID. Later eluting components from the BP-1 (approx. 12 minutes to 48 minutes) are detected directly by a second FID. The chromatograms obtained from a 600cc sample of a nominal 5ppbV, 75% RH retention standard canister are shown in Figure 3.

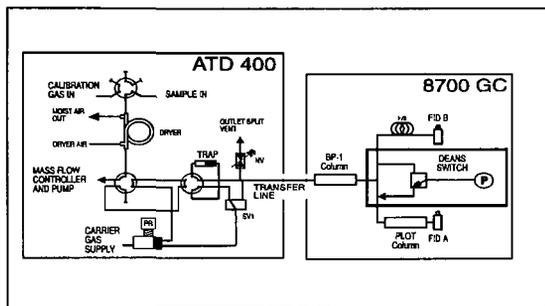


Figure 2. Cold Trap Desorption

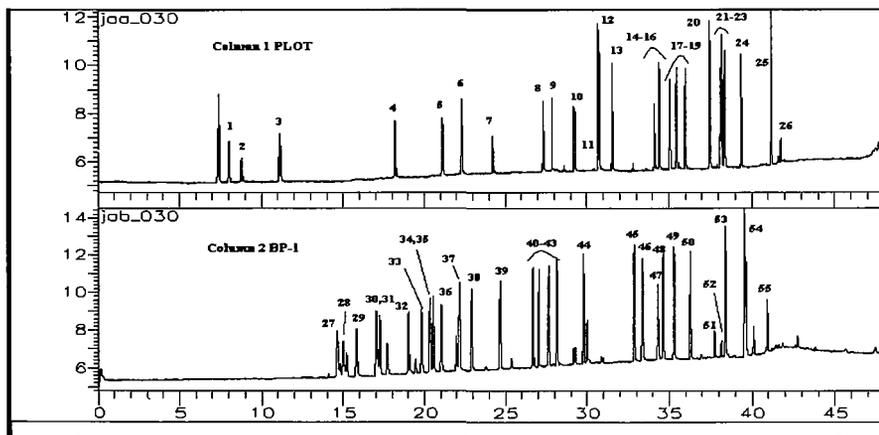


Figure 3. The 55-Components from the VOC List from Title 1 of the Clean Air Act

Initially a BP-5® (methyl 5% phenyl silicone) column was used for this work[6] to resolve the C<sub>6</sub> to n-C<sub>10</sub> hydrocarbons. However some important coelutions occurred resulting in the final selection of a non-polar methyl silicone column. In this chromatogram all components are resolved: the component identifications are listed below.

1 Ethane	11 Cyclopentane	21 3-Methylpentane
2 Ethylene	12 Isopentane	22 2-Methylpentane
3 Propane	13 n-Pentane	23 2,3-Dimethylbutane
4 Propene	14 2-Methyl-2-butene	24 Isoprene
5 Isobutane	15 Cyclopentene	25 4-Methyl-1-pentene
6 n-Butane	16 trans-2-Pentene	26 2-Methyl-1-pentene
7 Acetylene	17 3-Methyl-1-butene	27 n-Hexane
8 trans-2-Butene	18 1-Pentene	28 trans-2-Hexene
9 Isobutene	19 cis-2-Pentene	29 cis-2-Hexene
10 cis-2-Butene	20 2,2-Dimethylbutane	30 Methylcyclopentane

31	2,4-Dimethylpentane	40	2,3,4-Trimethylpentane	49	n-Nonane
32	Benzene	41	Toluene	50	Isopropylbenzene
33	Cyclohexane	42	2-Methylheptane	51	n-Propylbenzene
34	2-Methylhexane	43	3-Methylheptane	52	a-Pinene
35	2,3-Dimethylpentane	44	n-Octane	53	1,3,5-Trimethylbenzene
36	3-Methylhexane	45	Ethylbenzene	54	b-Pinene
37	2,2,4-Trimethylpentane	46	p-Xylene	55	1,2,4-Trimethylbenzene
38	n-Heptane	47	Styrene		
39	Methylcyclohexane	48	o-Xylene		

The C<sub>2</sub>s (ethane, ethene and acetylene) have the highest vapor pressure of the target analytes, and normally require large quantities of liquid nitrogen to trap and chromatograph them. Here ethane elutes at 8 minutes, ethene at 9 minutes and acetylene at 24 minutes and are thus well resolved. No liquid cryogen is used in this system. Separation of the 55 hydrocarbons is facilitated by the multidimensional column set. By ensuring that no compounds more volatile than hexane (in the elution order) are presented to the PLOT column this system, when operated continuously, provides optimum stability. (Note that in this system no component elutes on both columns.)

The chromatographic conditions used for this analysis were:

GC:	Initial Oven Temp.	46°C	ATD:	Column Head Pressure	48psi
	Initial Oven Time.	15min		Collection Time	40min.
	Ramp Rate	5degC/min.		Sample Collection Flow	15cc/min.
	Oven Temp.	170°C		Cold Trap Low Temp.	-30°C
	Ramp Rate	15°C		Cold Trap High Temp.	325°C
	Final Oven Temp.	200°C		Trap Hold at High Temp.	10min.
	Final Oven Time	6min.		Cycle Time	60min.
	Mid-point Pressure	21.5psi			

Trap Packing: 44mg Carbotrap<sup>®</sup> C/60mg Carbosieve<sup>®</sup> SIII

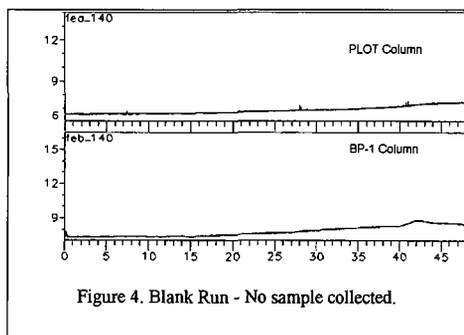


Figure 4. Blank Run - No sample collected.

Moisture management is by means of a semi-permeable membrane dryer, the performance of which has been described [8]. The analysis time is 48 min. The parameters have been carefully optimized to ensure that this system can meet its primary objective, viz.: a robust, turnkey system capable of long term continuous operation with the minimum of attention. It can be seen that, although all peaks of interest elute by 41 minutes, the run is extended to 200°C and held there for 6 minutes. This is to provide the PLOT column with a short bake which prepares it for the next analysis. Similarly, the ATD trap, once it is fired to 325°C, is held at that temperature for 10 minutes to prepare the sorbent bed for the next sample collection. By these means it is assured that there is no carryover from the trap and that optimum stability is obtained from the PLOT column. A second firing of the trap under such

circumstances is blank[5]. Figure 4 shows the chromatograms obtained when no sample is collected. In this case, the small low-boiling peaks obtained (e.g. 2mV methane) possibly represent residual sample diffusing through the sample collection system: no peaks are obtained in the region C<sub>6</sub> to C<sub>10</sub>.

Peak area repeatability for successive samples of calibrant is shown in Table 1. Retention time stability data from 105 hours of sequential sampling is shown in Table 2.

Table 1: Area Repeatability				
Name	Replicates	Mean	SD	%RSD
Ethane	8	76236	3574	4.69
Ethylene	8	69492	3378	4.86
Acetylene	8	47997	2779	5.79
1-Butene	8	118966	5743	4.83
Cyclopentane	8	150602	5071	3.37
1-Pentene	8	128217	3446	2.67
Benzene	8	298474	10300	3.45
Toluene	8	122969	4643	3.78
n-Octane	8	130084	2946	2.26
Ethylbenzene	8	54167	3309	6.11
p-Xylene	8	110158	4882	4.43
Styrene	8	106367	4069	3.83
Isopropylbenzene	8	121744	9252	7.60
1,3,5-Trimebenzene	8	140447	4586	3.27

Table 2: Retention Time Stability		
Name	Average RT	%RSD
Ethane	8.75	0.27
Ethylene	9.47	0.37
Acetylene	23.52	0.82
Butane	22.25	0.45
Isopentane	30.61	0.25
n-Pentane	31.44	0.24
1-Hexene	41.66	0.23
n-Hexane	14.07	0.23
Benzene	18.45	0.16
Toluene	26.63	0.10
n-Octane	29.48	0.07
Ethylbenzene	32.68	0.07
o-Xylene	34.47	0.06
1,3,5-Trimebenzene	38.85	0.07

### 5. System Timing for Hourly Analyses

The cycle time is 60 minutes, i.e., each run starts after exactly one hour - say 10 minutes after every hour. The temperatures and times are selected such that, even under worst case conditions, both the GC and the ATD are able to stabilize at their initial conditions prior to the next run (i.e., within the 60 minute envelope). The timing of the system is shown in Figure 5.

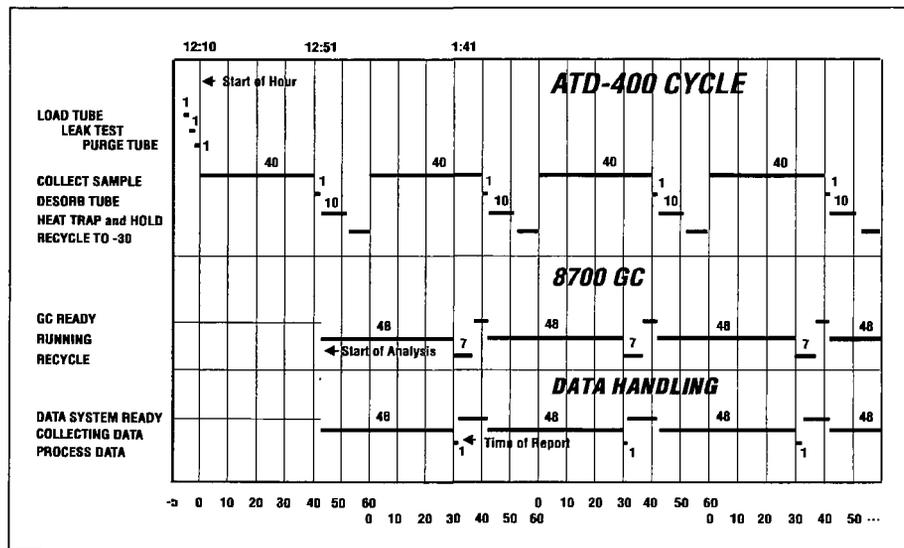


Figure 5. ATD-400 Ozone Precursor System Timing Diagram

The entire sample pathway is leak tested prior to collecting the first sample. Thereafter, a run is performed every 60 minutes. While a run is in progress a fresh sample is being collected. One such system has run 5300 hours on the same cold

trap, with an interruption of 56 hours after 2500 hours for firmware updates. At 5300 hours the glass wool used to retain the sorbent lost its flexibility and had to be replaced.

## 6. DESIGN CRITERIA FOR LONG TERM UNATTENDED OPERATION

### 6.1 Consumables

The consumable of most concern is *air* owing to the utilization of 800cc/min. by the dual FIDs, plus 250cc/min. by the Nafion® dryer, plus 20cc/min. by the ATD-400. A single tank of air lasts about 5 days. A tank of helium carrier gas lasts 3 months or more since the flow is only about 5cc/min., and hydrogen is consumed at the rate of 80cc/min. by the dual FIDs so a typical tank will last approximately 5 weeks. The design goal for this system was two weeks without a visit.

A special commercial zero-air generator equipped with a self-regenerating dryer (Balston Inc.) was used since it had a sufficient delivery rate (>1L/min.) to meet all the requirements of the system and provides air with a dew point of -100°C, making the Nafion® dryer more efficacious.

This approach suffers from a serious drawback in that it cannot survive a power failure since the FID flames go out as the air pressure drops. A stand-by air cylinder was installed teed into the air line as shown in Figure 6. By selecting suitable pressures as indicated on the diagram the air tank outlet is arranged to be normally just below the delivery pressure of the zero air generator and thus it stays off-line. If the pressure falls due to a loss of zero air the air tank will start to supply when its pressure exceeds the compressor pressure. When power is restored the air tank will take itself back off line after the zero air generator pressure rises. This simple arrangement does not require power. The receiver tank is included to neutralize pressure surges that might otherwise extinguish the flames.

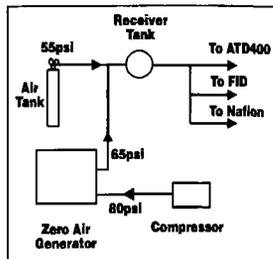


Figure 6. Air Supply Plumbing

### 6.2 Surviving Power Outages

Once the system was configured to survive a power outage and bring itself back on line, the next step was to ensure that the system would automatically restart sampling at the appropriate time after the top of the hour. This was done by putting a wait statement into the computer Autoexec.bat startup file. Thus the computer cannot restart until a stipulated time, at which point it allows the GC to come ready, which in turn allows the ATD-400 to resume sample collection. The first run following any power failure will therefore be a cleanup run, with the second or third run containing useful data depending on the period of the outage. A log is kept in the computer of all restarts.

### 6.3 Data Storage and Archival

The Turbochrom™ data handling system running under Windows® collects two channels of raw data per run at up to 70kbytes total (these are the chromatograms). In addition it is possible to create reports for each run of a further 11kbytes total. The operator will require ~20 preformatted 1.4Mb floppies to back up the data for two weeks. There is also the matter of data integrity for Quality Control/Quality Assurance purposes: if the raw data are written to the computer hard disk and there is a power outage with possible damage to the hard disk, the data are lost. To get around both of these issues we have elected to use external Bernoulli disk drives. A 90Mb Bernoulli disk drive will hold at least a month's worth of data. Access is as fast as a hard disk so it can be used by Turbochrom as a directory, unlike a tape cartridge which is purely a sequential archive device. The data are now recoverable, since in the unlikely event of a head crash the disk may be recovered using standard repair utilities. Most importantly, simply unplugging a full disk and replacing it with a preformatted blank disk is all that is required to archive 90 megabytes of data - which is superior to off loading onto a large number of floppies during a field visit. Alternatively, the data may be actively stored on the hard disk and archived periodically to the Bernoulli disk.

### 6.4 Remote Communications

Since the system is running largely unattended, it is likely that the system supervisor will wish to examine the chromatography of the system periodically. This is possible and convenient using high speed modems (Microm®, Model QX/4232bis+ MNP-10) with Norton PCAnywhere® communications software. This modem is rated for cellular service and is better able to tolerate poor quality phone lines. It is found that using regular phone lines access at 19,200 baud is possible using MNP protocol, with the convenience of remote mouse operation for the manipulation of the data display. Using PCAnywhere security features, the system can be programmed to call back only certain phone numbers thus limiting access by unauthorized callers. Scheduling software allows file transfers to be automated such that the bulk of the report data is transmitted at night on a daily basis to avoid peak calling periods.

## 7. CONCLUSIONS

An automated system has been designed for the hourly detection of the Ozone Precursor compounds stipulated under the Clean Air Act. Since Peltier cooling is used to trap the VOC species no liquid cryogen is required. Operation for a two week unattended period is possible by configuring gas supplies for continuous operation. Optimum stability, coupled with enhanced resolution of the C<sub>2</sub> compounds is achieved by multidimensional chromatography. The system may be accessed and files transferred using high speed data communications. Automatic recovery in the event of a power failure ensures the maximum data capture rate for remote installations.

## References:

1. US. Environmental Protection Agency, Code of Federal Regulations, Title 40 Part 58, Enhanced Ozone Monitoring Regulations, October 1991.
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## ACKNOWLEDGMENT

The ATD-400 On-Line Air Monitoring Capability and Ozone Precursor Application was developed by the Perkin-Elmer Corporation in collaboration with the US EPA Exposure and Assessment Laboratory under an FTTA agreement.

## Trademarks:

PLOT	Chrompack BV
Carbosieve	Supelco Inc.
Carbotrap	Supelco Inc.
Turbochrom	Perkin Elmer Corp.
Microcom	Microcom Corp.
PCAnywhere	Norton/Symantec
BP-1,BP-5	SGE Corp.
Windows	Microsoft Corp.
Nafion	Permapure Inc.
Bernoulli	Iomega Corp.

## **Field Monitoring of Ozone Precursors Using An Automated Gas Chromatographic System.**

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### **ABSTRACT**

Title I, Section 182 of the 1990 Clean Air Act Amendments requires states in ozone non-attainment areas to establish photochemical assessment monitoring stations (PAMS) which include monitoring for ozone precursors. During the summer of 1992, Delaware was one of three states along the Northeast Corridor to evaluate the Chrompack automated gas chromatograph in the field. Air samples were taken through a manifold, concentrated cryogenically, and analyzed for target volatile organic compounds by capillary gas chromatography with FID detection. This paper will discuss Delaware's preliminary assessment of the system and initial results.

### **DISCLAIMER**

Although the research described in this paper has been funded in part by the U.S. Environmental Protection Agency (EPA), it has not been subjected to EPA's peer and administrative review; it does not necessarily reflect the view of the Agency and no official endorsement should be inferred.

## INTRODUCTION

On March 4, 1992 the proposed rule to revise the ambient air quality surveillance regulations to include provisions for the enhanced monitoring of ozone and its precursors was published in the Federal Register<sup>1</sup>. These regulations addressed the minimum requirements for the monitoring of speciated volatile organic compounds (VOC), oxides of nitrogen (NO<sub>x</sub>), and meteorological parameters.

In accordance to the proposed rule, Delaware Department of Natural Resources and Environmental Control, Air Surveillance Branch established a Type 1 PAMS which characterizes upwind background and transported ozone precursor concentrations entering the Philadelphia Consolidated Metropolitan Statistical Area (CMSA). The station is located at Lums Pond State Park which is approximately 9 miles southeast from downtown Wilmington. The 8 x 12 foot (ft) shelter is equipped with a Chrompack VOC Air Analyzer, Dasibi ozone analyzer and a Monitor Labs NO/NO<sub>2</sub>/NO<sub>x</sub> analyzer. Meteorology data was obtained from the National Weather Service located at the Greater Wilmington airport during this study.

## EXPERIMENTAL METHODS

Ambient air was sampled 34 minutes during each hour for a minimum of 24 hours, once a week from June to August 1992. A Chrompack pump unit was used to draw air from the manifold. This unit included a mass flow controller to control sample flow and a Perma-Pure dryer system to selectively remove water.

The sample was collected and preconcentrated onto a Carbotrap C/Carbotrap/Carbosieve adsorption tube (75mm by 6mm OD by 3mm ID) at a 10 ml/min flow rate. The primary trap was cooled to -21°C using liquid nitrogen. After desorption from this trap at a temperature of 250°C, the sample was transferred to the Poraplot U fused silica trap (0.53mm ID, 20 um film thickness) for cryogenic focusing of components. Liquid nitrogen was used to cool the secondary trap to -105°C. The cold trap was flash heated to 140°C and then injected onto the column. The cycle of collection, concentration, drying, desorption, trapping and injection was completely automated and controlled by the Chrompack auto TCT unit.

A single Al<sub>2</sub>O<sub>3</sub>/KCl PLOT capillary column 25m by 0.32mm ID was used for separation. The column temperature program had an initial temperature of 50°C for 2 min, a rise of 5°C/min up to 75 °C, 10°C/min up to 125°C, 15°C/min up to 200°C, and a final temperature of 200°C for 30 minutes. The carrier gas was ultra pure grade helium. Analyses of the samples were performed on a Chrompack CP-9000 GC with a single flame ionization detector. Data acquisition utilized the Chrompack PCI software. Results were both printed out and also stored on the hard drive and then transferred to a 3.5 floppy disk.

A 60 component standard supplied by Radian was used for retention time calibration. A 1% window was set for compound identification. Single point calibration using benzene as a standard was done to determine the response factor.

## RESULTS

49 of the 60 VOCs in the calibration standard were separated and tentatively identified.

methylhexane occurred as one peak as did 2&3- methylheptane and m/p-xylene. Out of 6 calibration runs, the coefficient of variation for retention times ranged from a low of 0.13% for ethane to a high of 0.68% for n-propyl-Benzene (Table 1). 42 of the 52 target VOC peaks were detected in the ambient air during the sampling period. These 42 made up 72.75% of the total measured VOCs. The maximum value measured was above 10 ppbC for the following compounds: propane, n-butane, 2-methylbutane, n-hexane, 2&3-methylheptane, n-octane, toluene, m/p-xylene and 1,3,5-trimethylbenzene. The maximum value measured was between 5 and 10 ppbC for the following compounds: ethane, propene, acetylené, isobutane, isobutene, n-pentane, 2&3-methylhexane, benzene, and 2,3,4-trimethylpentane. The maximum measured value was between 1 and 5 ppbC for the following compounds: ethene, isobutane, trans-2-butene, cis-2-butene, cyclopentane, 2-methyl-2-butene, methylcyclopentane, 2,3-dimethylbutane, 2-methylpentane, 3-methylpentane, isoprene, 3-methylpentene, 2,3-dimethylpentane, 2,4-dimethylpentane, methylcyclohexane, n-heptane, perchloroethylene, nonane, ethylbenzene, o-xylene, and isopropylbenzene. The maximum measured value was less than 1 ppbC for the following compounds: trans-2-pentene, pentene, and trichloroethene. The following compounds were not detected: 1-butene, 3-methyl-1-butene, 2-methyl-1-butene, cis-2-pentene, cyclohexane, trichloromethane, trans-2-hexene, 2-methyl-1-pentene, cis-2-hexene and n-propylbenzene. Averaging all of the sample data, the 10 most abundant compounds on a carbon basis were in order of abundance: propane, isobutene, toluene, ethane, 2-methylbutane, n-butane, trans-2-butene, n-hexane, acetylene and benzene. These 10 compounds made up 53.91% of the total measured VOCs ( Table 2). Total measured VOCs ranged from 25 to 199 ppbC with a mean of 58 ppbC. Averaging total VOCs per time of day, total measured VOCs reached the highest level at 0900 (Figure 1).

## DISCUSSION

Approximately 50 runs could be obtained using one 160 liter dewar of liquid nitrogen. Use of liquid nitrogen at a field site in this size container caused logistical problems. Due to a state contract the exact time of delivery could not be specified. On occasion containers were delivered several days early and lost much of their contents before they were used. Man-hours necessary to maintain the system were higher than anticipated due to the frequent need to check on or change the liquid nitrogen container. Sampling was not done over the weekend because it would have required someone to change the liquid nitrogen container on the weekend and there were no funds for overtime pay. Delivery of cylinders to a site that was not always occupied also caused occasional problems. Expected deliveries were not received when drivers unfamiliar with the site did not know the combination to the enclosure, arrived in a truck too large to fit on site, and dropped off the wrong order. Once the cylinders were received, ease of movement was facilitated by a concrete walkway along the side of the station.

The EPA Technical Assistance Document<sup>2</sup> encourages the use of a less complex single-column configuration to perform the initial system set-up and optimization. This approach worked quite well and is recommended for the less experienced chromatographer. The Chrompack Al<sub>2</sub>O<sub>3</sub>/KCl PLOT column provided good separation of the light hydrocarbons but many of the peaks for the C<sub>5</sub> - C<sub>8</sub> range were very close together and difficult to identify. Some C<sub>9</sub> hydrocarbons could be identified but the peaks were very broad. A second column is recommended to confirm analytical results.

On 4 occasions power interruptions to the station occurred during the sampling period. When this occurred the system went into the standby mode and did not continue sampling when the power resumed. 51 hours of intended sampling time were lost because of this. To remedy this

problem in the 1993 sampling season, an un-interruptible power supply has been purchased.

Sampling time was also lost due to a missing ferrule on the pump unit when the instrumentation was moved from the laboratory to the field station. This caused a major air flow leak into the system. Hardware down time occurred when the main fuse was blown. The system status indicated " Motor Off ". This was resolved as soon as the fuse was replaced. Detailed recorded keeping is a must for this type of system. It will be used for both trouble shooting the hardware and also to provide quality in the data.

The PCI software was used in operation control of the automated GC system and for hourly data analysis and information storage but was not useful for overall statistical analysis between groups of the hourly files. Additionally the software occasionally appeared to fail to identify compounds that were within the window limits. The need for better software was very evident. For the 1993 season our agency has purchased the Chrompack Mosaic software.

The 8 x 12 ft shelter was barely adequate in size. It was inconvenient when more than one person was working within the station or when work which required access behind the instruments needed to be done.

## CONCLUSIONS

In a preliminary study, an automated GC system located at a field site was used to analyze ambient air samples for VOCs. 10 compounds made up 53.91% of the total measured VOCs. The mean of the total measured VOCs peaked at 0900. Problems with the system included frequent need to monitor liquid nitrogen use, complete shutdown of the system due to momentary power losses, and the need for better software. Advantages to the system include hourly data, good separation of the light hydrocarbons, and minimum variability between calibration runs.

Further technical development needs to address hardware improvements, analytical method research and development, and quality assurance and quality control.

## ACKNOWLEDGEMENTS

The authors wish to express their appreciation to Delaware 's Division of Parks and Recreation for providing the availability of land for the PAMS site at Lums Pond State Park and also to the United States Environmental Protection Agency at Region III for both their financial and technical support in this project.

## REFERENCES

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2. Technical Assistance Document for Sampling and Analysis of Ozone Precursors, EPA/600-8-91/215, U.S. EPA, Research Triangle Park, NC, October, 1991, p 2-15.

Table 1. Mean Retention Times for Calibration Runs

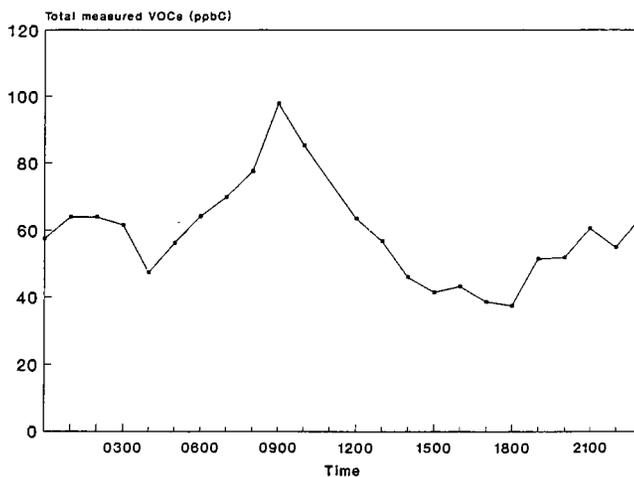
Compound	RT mins	SD	CV %	Compound	RT mins	SD	CV %
ethane	1.813	0.002	0.132	n-hexane	14.007	0.020	0.144
ethene	1.783	0.004	0.204	trichloromethane	14.407	0.029	0.204
propane	2.348	0.008	0.323	3-methylpentene	14.883	0.027	0.184
propene	3.856	0.018	0.496	trans-2-hexene	14.711	0.027	0.187
acetylene	4.690	0.024	0.503	2-methyl-1-pentene	14.783	0.028	0.186
l-butane	4.812	0.031	0.652	cis-2-hexene	15.315	0.027	0.174
n-butane	5.137	0.026	0.509	trichloroethene	15.561	0.025	0.181
trans-2-butene	7.721	0.034	0.443	2,3-dimethylpentane	15.751	0.029	0.181
1-butene	7.886	0.034	0.428	2,4-dimethylpentane	15.909	0.032	0.204
l-butene	8.388	0.032	0.384	methylcyclohexane	16.074	0.029	0.182
cis-2-butene	8.780	0.033	0.372	2&3-methylhexane	16.146	0.027	0.170
cyclopentane	9.431	0.033	0.349	n-heptane	16.494	0.029	0.174
2-methylbutane	9.560	0.036	0.372	perchloroethylene	16.663	0.026	0.158
n-pentane	10.052	0.032	0.320	benzene	17.102	0.029	0.170
3-methyl-1-butene	11.364	0.028	0.249	2,2,4-trimethylpentane	17.910	0.037	0.209
trans-2-pentene	11.671	0.027	0.234	2,3,4-trimethylpentane	18.332	0.041	0.225
2-methyl-2-butene	12.008	0.027	0.222	2&3-methylheptane	18.559	0.043	0.233
pentene	12.074	0.027	0.224	n-octane	19.046	0.046	0.244
2-methyl-1-butene	12.219	0.027	0.219	toluene	20.116	0.059	0.296
cis-2-pentene	12.437	0.026	0.206	nonane	23.429	0.109	0.464
methylcyclopentane	13.029	0.036	0.279	ethylbenzene	24.753	0.127	0.511
cyclohexane	13.229	0.043	0.323	m/p-xylene	25.289	0.128	0.505
2,3-dimethylbutane	13.330	0.026	0.195	o-xylene	27.193	0.147	0.541
2-methylpentane	13.397	0.027	0.202	isopropylbenzene	30.006	0.176	0.587
3-methylpentane	13.470	0.028	0.206	n-propylbenzene	30.820	0.209	0.883
isoprene	13.816	0.029	0.207	1,3,5-trimethylbenzene	34.086	0.226	0.664

Table 2. Ten most abundant compounds

Compound	Mean Concentration (ppbC)	Standard Deviation	% of total VOCs
Propane	6.09	8.52	10.43
I-Butene	6.01	1.81	10.30
Toluene	3.07	2.30	5.26
Ethane	2.98	1.42	5.11
2-Methylbutane	2.92	2.96	5.01
n-Butane	2.39	2.53	4.10
trans-2-Butene	2.18	1.42	3.74
n-Hexane	2.10	2.54	3.60
Acetylene	2.10	1.25	3.59
Benzene	1.62	1.21	2.77
Total VOCs	58.38	30.78	100.00

1992 Data

Figure 1. Total measured VOCs vs Time



Average of 1992 data

## PERFORMANCE EVALUATION OF THE HP-5971A MSD FOR ANALYSIS OF VOCs IN AIR

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### ABSTRACT

The analysis of volatile organic compounds in air by GC/MS using the Hewlett-Packard Model 5971A Mass Selective Detector (MSD) has been evaluated over the past 18 months. The analytical methods used for VOC analyses were TO-14, TO-1, TO-2 for ambient air samples, IP-1A and 1B for indoor air samples, and the VOST and Method 18 for source test methods. Practical quantitation limits for the 60 VOCs were 5 ng on-column, which ranges from 1 to 2 parts per billion by volume, in the full scan mode. Precision and accuracy was determined by replicate analyses, and interlaboratory comparisons of audit gases. For six audit canisters (three analyzed one year, and another three analyzed a year later), the average accuracy or bias was 92%, and the average precision (% RSD) for 19 volatile organic compounds was 24%.

### INTRODUCTION

Volatile organic compounds are being measured in air to determine emissions from chemical processes, materials, landfills, and control equipment. VOC measurements are also needed to determine air pathways, and exposure assessments in ambient and indoor air environments. Samples are collected in Tedlar bags, Tenax and charcoal sorbents, passivated stainless steel containers, and are analyzed on-site or shipped to the laboratory for analysis. The HP-5970 mass selective detector has been used successfully for many years for analysis of VOCs in air, and was upgraded by the introduction of the HP-5971A model. Several changes that were made were replacing the pumping system from a turbo-molecular to a diffusion pump, reducing the physical size of the detector, reducing the mass range from 800 amu to 650, and upgrading the HP ChemStation software to a MS-DOS personal computer system. With the lower cost 5971A model, and its compact size, it became a very attractive instrument for laboratories to consider for environmental analyses. Our laboratory purchased a 5971A MSD with the MS-DOS system for air toxics analyses, and have summarized the performance for VOC analyses. The objectives of our evaluation were to determine VOC in air analysis precision and accuracy, practical quantitation limits in the full scan electron impact mode, its adaptability to modifications, and the system's ease of use and maintenance requirements under daily routine use.

### EXPERIMENTAL

The 5971A MSD we purchased was the most recent version, which had been improved by Hewlett-Packard by adding vent holes to the ion source and upgrading the mother board. The MSD was added to an existing HP-5890 gas chromatograph which was connected to a modified Tekmar LSC-2000 purge and trap concentrator used to concentrate and introduce air samples to the GC. The canister, Tedlar bag, or VOST cartridges were connected to a heated stainless steel transfer line, 1/16 in. OD, using a leak tight fitting. The LSC purge line was disconnected from the glass purge vessel, to provide purge gas for VOST samples, and the transfer line from the air sample was connected directly to the purge vessel. This configuration allowed the sample to enter the purge vessel and then concentrate onto the trap in the Tekmar apparatus. With VOST and TO-1 Tenax cartridges, a clam shell type desorption heater was used to thermally desorb the VOCs through the heated transfer line. For canisters and Tedlar bag samples a known amount of sample (usually 0.5-1 liter) was concentrated onto the carbon molecular sieve trap in the Tekmar LSC-2000. The sample flow rate was controlled with a Porter mass flow controller and a vacuum pump connected at the vent side of the Tekmar unit. The concentrated sample was then thermally desorbed onto a fused silica capillary column.

#### Tekmar LSC-2000 Conditions:

Purge time: 10 min at 50 mL/min  
Valve Temp: 200°C  
Bake out Temp: 270°C

Mount, Transfer Temp: 110°C, 150 °C  
Desorb Temp: 250°C for 3 min at 10 mL/min  
Trap: Carboxpack B, 7.6 cm/Carbosieve S-III, 1.3 cm

#### GC/Mass Selective Detector Conditions:

Transfer Interface Temp: 250°C  
Oven: -50°C for 2 min programmed to 220°C @ 8°C/min  
Column: 30m x 0.53mm 3 u, DB-624; He flow rate: 10 mL/min,  
SGE Megabore Stainless Steel Jet Separator  
Full Scan Mode: 35-260 AMU  
HP ChemStation MS-DOS 1990 Ver. 4 Software with Microsoft Excel

A calibration curve consisting of 10 ng, 50 ng, 100 ng, 200 ng, 500 ng, and 1000 ng was constructed by injecting aliquots of each analyte (Table 1) into the concentrator purge vessel during the purge cycle. Certified standard mixtures obtained from Absolute Standards at 2000ng/uL in methanol solvent were used. 200uL of the target compound mixture was injected into a 2.0 liter static dilution bulb containing ultra pure nitrogen. The resulting concentrations were 200ng/mL of gas. The internal standard method of calibration was used for all target compounds. The following internal standards were used: 1) 1,4-difluorobenzene, 50ng; 2) *d*<sub>5</sub>-chlorobenzene, 50ng. The following surrogate compounds were used to determine injection recoveries: 1) bromochloromethane, 50ng; 2) *d*<sub>2</sub>-1,2-dichloroethane, 50ng; 3) *d*<sub>8</sub>-toluene, 50ng; 4) 4-bromofluorobenzene, 50ng. Preparation of the internal standard and surrogate standard gas mixture was done by injecting 200uL of a 1000ng/uL certified stock solution from Ultra Scientific into a 2.0 liter static dilution bulb containing nitrogen. The resulting concentrations were 100ng/mL of gas. One-half mL of this standard was injected with each sample and target standard mixture. The automatic macro quantitative calculation program in the HP ChemStation software was setup to calibrate using the internal standards and calculate unknown analytes using the average response factor determined from all points.

## RESULTS AND DISCUSSION

The system was tuned daily using BFB and has had no problems meeting the EPA acceptance criteria. Operator use has been easy, and maintenance has been extremely low. EPA performance audits in SUMMA® canisters had acceptable precision of 24%, and an accuracy of 92%, at levels of 1-20 ppbv (Table II). Audit results of Tenax cartridges (Table III) loaded with 13 compounds in the range of 100 ng to 800 ng demonstrate that average recoveries of 88%, with a standard deviation of 20 can be achieved. Figure 1 presents results of the 1,4-difluorobenzene internal standard, and the surrogate standard recovery plots over 48 injections. The internal standard had an %RSD of 16.3 over a period of three weeks, and the second internal standard (*d*<sub>2</sub>-dichlorobenzene), which is not shown here, performed almost the same with a %RSD of 20.8. The surrogate standards had the following acceptable recoveries, and %RSD's: bromochloromethane, 92%, 7.6; *d*<sub>2</sub>-1,2-dichloroethane, 100%, 8.3; *d*<sub>8</sub>-toluene, 102%, 5.4; bromofluorobenzene, 97%, 8.9. Additional precision, accuracy, and SUMMA® canister stability results of 21 VOCs at 5 ppbv are presented in Table IV. The atmospheric pressure 6-liter audit canister was analyzed over a 60 day period with an average recovery of 97.2%, with a standard deviation of 19.7.

One problem that occurred and was resolved was the effects of moisture. Common to quadrupole mass spectrometers is the suppression effects of water in the ion source. The water was not a problem in most ambient air samples using the Carboxpack B/Carbosieve SIII sorbent focusing procedure because of its hydrophobic characteristics. The very small amount of water that did enter the source did not interfere with any analytes of interest. Unfortunately, the audit samples were fortified with large amounts of water, that co-eluted with the 1,4-difluorobenzene internal standard, and took all day to come back to acceptable levels in the MSD. The effects were a 20% reduction of response of the internal standard, but not to the target compounds, which incorrectly adjusted the analyte values to a higher amount. A 4 min. dry purge was added to our procedures, and removed sufficient water to maintain consistent responses. We also recalculated the analyses that showed water effects, using the external standard procedure, with acceptable results. This further proves the water was the cause of the high recoveries. Further work should be done to fully evaluate the effects of water and to establish guidelines in dealing with the potential errors involved. Although we experienced a few problems, we found the system met our performance specifications, and expectations.

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**Table I. VOCs on HP-5971A Mass Selective Detector.**

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The following compounds have practical quantitation limits of 1 ppbv in SUMMA\* canister air samples analyzed in the full scan mode.

Dichlorodifluoromethane	Tetrachloroethene
Chloromethane	1,1,2-Trichloroethane
2-Methyl-1-Propene	Bromoacetone
Vinyl chloride	2-Hexanone
Bromomethane	Dibromochloromethane
Chloroethane	1,2-Dibromoethane
Trichlorofluoromethane	Chlorobenzene
1,1-Dichloroethene	1,1,2,2-Tetrachloroethane
Iodomethane	Ethyl benzene
Carbon Disulfide	o, m, p-xylenes
Acetone	Nonane
Acetonitrile	Styrene
Methylene chloride	Bromoform
Trans-1,2-dichloroethene	Cumene
2-Methyl-2-Propanol	1,2,3-Trichloropropane
Hexane	1,4-Dichloro-2-butene
1,1-Dichloroethane	1,1,2,2-Tetrachloroethane
Vinyl Acetate	Pentachloroethane
2-Butanone	1,3-Dichlorobenzene
Chloroform	1,4-Dichlorobenzene
1,1,1-Trichloroethane	1,2-Dichlorobenzene
Carbon tetrachloride	1,2-Dibromo-3-chloropropane
1,2-Dichloroethane	
Benzene	
Fluorobenzene	
Heptane	
2-Chloro-2-Methylpropane	
Trichloroethene	
1,2-Dichloropropane	
Dibromomethane	
1,4-Dioxane	
Bromodichloromethane	
cis-1,3-Dichloropropene	
4-Methyl-2-Pentanone	
Toluene	
trans-1,3-Dichloropropene	

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Based on a 500 mL air sample

Table II. EPA Canister Audit Results, 1992 and 1993.

Canister # ng/L	519 Loaded	% Rec	484 Loaded	% Rec	A06 Loaded	% Rec	711 Loaded	% Rec	709 Loaded	% Rec	740 Loaded	% Rec
Vinyl chloride	3.5	97.1	4.1	85.4	11.4	105.3	11.7	123	51.3	119.4	25.1	108.9
Bromomethane	5.6	89.3	6.5	78.5	18.2	78.0	15.9	98.9				
Trichlorofluoromethane	8.8	34.4	70.8	28.3			25.2	100				
Methylene chloride	5.0	66.0	5.8	69.0	16.1	98.8	7.0	151				
t-1,2-dichloroethene	5.5	101.8	6.4	104.7	17.9	101.7	7.9	128				
1,1-dichloroethane	6.6	78.8	7.5	77.3	21.2	59.0	20.0	99.0				
Chloroform	7.2	90.3	8.2	89.0	23.1	87.0	23.2	99.0	117	87.5	57.1	92.4
1,1,1-trichloroethane	8.1	90.1	9.3	89.2	26.0	62.3	28.8	66.6				
Carbon tetrachloride	8.6	96.5	9.9	92.9	27.7	92.8	28.0	41.1	66.1	56.2	32.3	48.7
Benzene	5.1	107.8	5.8	103.4	16.3	93.9	7.7	108	93.5	86.8	45.7	94.5
Trichloroethene	8.7	97.7	10.0	121.0	28.0	125.4	25.4	98.6				
1,2-dichloropropane	7.4	89.2	8.5	85.9	23.9	84.5	11.3	94.1				
Toluene	6.2	101.6	7.1	104.2	20.0	80.5	15.2	136				
Tetrachloroethene	11.0	70.0	12.7	72.4	35.6	71.3	31.8	95.3	52.2	77.0	25.6	82.9
1,2-Dibromoethane	11.3	74.3	13.0	73.1	36.4	73.6	25.1	76.9				
Chlorobenzene	7.5	82.7	8.6	81.4	24.1	78.0	10.5	98.8				
Ethyl benzene	7.1	85.9	8.1	81.5	22.7	82.8	10.1	104				
o-xylene	18.7	147.1	10.0	138.0	28.2	138.3	11.9	79.6				
Styrene	2.1	128.6	2.5	120.0	6.9	115.9	3.0	132				
<b>Average Recoveries</b>		<b>94.2</b>		<b>92.6</b>		<b>90.5</b>		<b>104</b>		<b>85.4</b>		<b>85.5</b>
<b>Standard Deviations</b>		<b>19.7</b>		<b>19.0</b>		<b>21.1</b>		<b>25.8</b>		<b>22.8</b>		<b>21.8</b>
<b>% RSD</b>		<b>20.9</b>		<b>20.5</b>		<b>23.3</b>		<b>24.8</b>		<b>26.7</b>		<b>23.8</b>

% Rec is percent recovery; 1992 audits were: # 519, # 484, # A06; 1993 audits were: # 711, # 709, # 740.

Table III. EPA Tenax Cartridges Audit Results.

Tenax Cartridge # Fall 1992	A-122		A-117		A-118		Average Recoveries
	ng Loaded	% Rec	ng Loaded	% Rec	ng Loaded	% Rec	
Chloroform	97	63	159	70	372	66	67
1,1,1-Trichloroethane	131	56	212	67	504	53	59
1,2-Dichloroethane	123	74	199	82	473	75	77
Carbon tetrachloride	156	77	240	91	625	88	85
Benzene	172	75	278	82	662	73	77
Trichloroethene	191	68	309	74	735	72	71
1,2-Dichloropropane	75	85	122	94	290	91	90
Toluene	198	101	320	102	761	91	98
Tetrachloroethene	159	95	257	104	611	103	100
Chlorobenzene	217	92	350	97	834	91	93
Ethyl benzene	142	113	229	120	544	115	116
o-Xylenes	172	126	278	131	663	124	127
<b>Average Recoveries</b>		<b>85</b>		<b>93</b>		<b>87</b>	<b>88</b>
<b>Standard Deviations</b>		<b>21</b>		<b>19</b>		<b>20</b>	<b>20</b>

% Rec is percent recovery.

Figure 1. Internal Standard Response and Surrogate Recoveries.

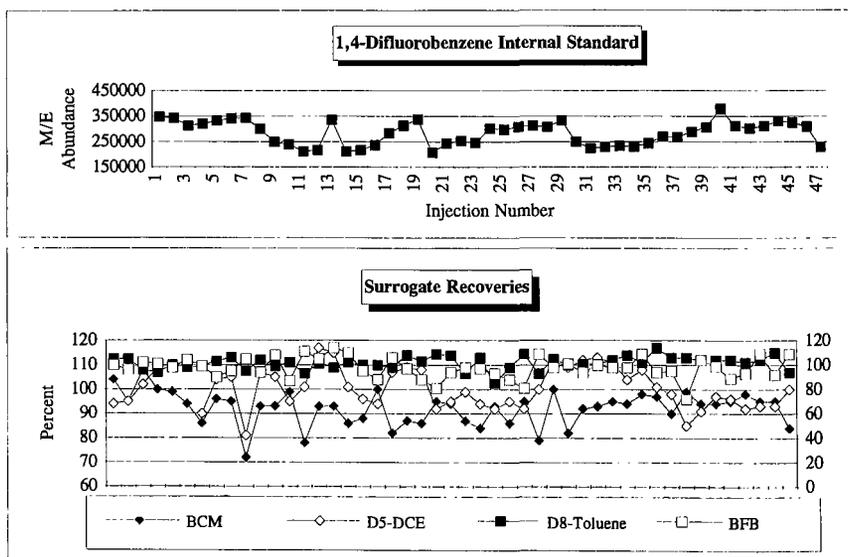


Table IV. Precision, Accuracy, and Stability of VOCs in a SUMMA Canister Over 60 Days

Date Analyzed	3/1/93	3/11/93	3/11/93	3/17/93	4/5/93	4/16/93	4/29/93						
Elapsed Days	Day 1	Day 10	Day 10	Day 16	Day 36	Day 47	Day 60						
Canister # 745 @ 5 ppbv											Mean		
March 1-April 29, 1993											% Rec		
Atmospheric press.	ng/L	ng/L Found						df:1.7	df:1.7	Mean	Stdev	%RSD	vs Load
	Loaded												
Vinyl chloride	11.2	14.0	14.0	14.0	15.0	10.5	11.4	13.2	1.7	13.2		117.6	
Bromomethane	17.9	19.6	19.6	20.0	19.0	18.4	16.7	18.9	0.6	3.3		105.3	
Trichlorofluoromethane	27.9	28.6	28.2	28.0	32.0	28.4	33.3	29.8	1.7	5.6		106.7	
1,1-dichloroethene	19.8	20.1	17.6	18.0	22.0	17.8	19.6	19.2	1.9	10.0		97.1	
Methylene chloride	15.9	16.3	15.5	16.0	19.0	17.3	17.8	17.0	1.4	8.1		107.1	
t-1,2-dichloroethene	17.6	18.3	18.1	19.0	19.0	18.9	17.3	18.4	0.4	2.4		104.8	
1,1-dichloroethane	20.8	18.8	17.8	18.0	19.0	19.7	18.0	18.5	0.8	4.2		89.0	
2-butanone	4.2	4.6	3.9	4.6	7.4	6.0	7.5	5.7	1.4	24.7		133.6	
Chloroform	22.7	24.1	23.4	23.0	24.0	23.8	21.0	23.2	0.5	2.0		102.1	
1,1,1-trichloroethane	25.6	26.8	25.2	27.0	30.0	25.1	24.3	26.4	2.0	7.5		103.1	
Carbon tetrachloride	27.3	18.9	18.3	11.0	0.0	0.0	0.0	8.0	9.3	116.2		29.4	
Benzene	16.1	15.3	14.3	15.0	18.0	16.2	16.0	15.8	1.4	9.1		98.4	
Trichloroethene	27.6	25.2	23.7	24.0	29.0	25.7	21.4	24.8	2.1	8.5		90.1	
1,2-dichloropropane	20.1	20.7	19.0	21.0	22.0	22.6	19.5	20.8	1.4	6.6		103.8	
Toluene	19.7	17.8	16.9	18.0	22.0	20.9	16.7	18.7	2.2	11.8		95.1	
Tetrachloroethene	35.1	33.4	32.0	32.0	37.0	32.6	30.7	33.0	2.1	6.3		94.0	
1,2-Dibromoethane	35.9	36.3	34.3	34.0	41.0	32.7	31.9	35.0	3.3	9.3		97.7	
Chlorobenzene	23.7	22.4	21.4	22.0	25.0	22.1	16.6	21.6	1.4	6.5		91.0	
Ethyl benzene	22.4	23.1	20.8	20.0	24.0	20.6	20.2	21.5	1.7	8.1		95.8	
o-xylene	27.7	21.6	20.9	18.0	21.0	19.0	17.6	19.7	1.5	7.8		71.0	
Styrene	6.8	8.0	7.0	6.8	8.7	7.2	6.6	7.4	0.8	10.6		108.1	
<b>Average</b>												<b>97.2</b>	
<b>Standard Deviation</b>												<b>19.7</b>	

df: dilution factor; % Rec: percent recovery

**Whole Air Analysis For TO-14  
Low Level And High Level Samples**

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**ABSTRACT**

A description of the design and operation of a cryoconcentrator for the Whole Air Analysis of TO-14 is discussed. Data is presented showing the precision (RSD's) of high level (source) and low level (ambient) samples and system blanks. Emphasized is the ability of the instrumentation to recover from both high and low level samples.

## INTRODUCTION

This talk will address instrumentation designed to accommodate the variety of sample types occurring in today's TO-14 whole air analysis. Whole air analysis refers to the whole or entire air sample compound set. This contrasts with analyses performed by sorbent approaches whereby, potentially, part of the sample can be missing. The specific sample set we will examine in this study is that of TO-14 which consists primarily of halogenated hydrocarbons.

## BODY

Today, Mother Nature gives us approximately 20ppbv of these TO-14 molecules in ambient air (consequently, the 2ppbv to 50ppbv calibration range for TO-14). However, special situations can occur to cause ambient concentrations to be dramatically higher — the sampling may include source (high level) material or sample containers may inadvertently be switched in the laboratory. The complication of mixing source and ambient samples is that concentrations may be different by many orders of magnitude. With prior knowledge, the careful analytical chemist will group his samples by both concentration and type. While this will not prevent an accidental mix-up, this approach will minimize the effect of carryover or cross contamination. Ideally, the analytical system employs a well-engineered design for addressing these real life complications. The first part of this talk will discuss such a design, and the second part will show the results from a TO-14 analytical set illustrating the effectiveness of this design.

One approach, in principle, to an effective design is to provide a high level (source) sample analysis pathway that is separate from the low level (ambient) sample analysis pathway. The analyst could then channel known source samples through the high level flow path and ambient samples through the low level flow path. This design offers the flexibility of screening all samples as if they were source samples, and the apparently ambient samples could be then analyzed through the low level flow path. Even with this approach, cleanup between samples is required to minimize cross contamination. Cleanup that is continuously in operation provides a maximum of recovery. The following flow schematics show such a system and how it processes high and low level samples while maintaining a continuous purging to ensure a maximum of recovery capability.

<Ten slides showing the flow operation of  
the Nutech Model 3550A Cryogenic Concentrator>

Theory of design is proven by actual sample determinations. The following data will show high level samples followed by blanks, low level samples followed by blanks, and RSD's. A TO-14 sample will, of course, contain compounds other than TO-14 species. These sample runs contain TO-14 compounds plus "interfering" compounds.

<Seventeen slides showing chromatograms and tables of data>

## CONCLUSIONS

The instrumental design discussed here has established, through the data presented, the capability of analyzing the wide variety and concentrations of TO-14 samples challenging the environmental laboratories today.

## REFERENCES AND BIBLIOGRAPHY

None cited.

***Session 17***  
***Acid Aerosols***  
***and Related Pollutants***

**ACID AEROSOL MEASUREMENT METHODS:  
A SUMMARY OF U.S. EPA INTERCOMPARISONS**

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**ABSTRACT**

Studies of human exposure to acid aerosols have been underway for several years, leading to the need to intercompare measurement methods for acidic aerosol concentrations. Over the past few years the U.S. EPA has sponsored several intercomparisons of the methods in use. Most of these methods are similar; nevertheless, some differences exist among the samplers, as well as in details of their operation. The studies have included single component aerosols of sulfuric acid and ammonium bisulfate, photochemical aerosols, a sequence of compounds chosen to test for on-filter neutralization by ammonium nitrate, the addition of alkaline dust, laboratory-spiked samples, and atmospheric aerosol samples. These studies were designed to establish both intra- and interlaboratory precision and to attempt to separate the effects of differences in flow rate, extraction, and analysis. All major groups that are active in acid aerosol measurement have participated. These studies have not been done for the purpose of choosing a best method, but rather to document the current level of performance and to suggest items for improvement. The results of these studies are that intralab precision (stated as the coefficient of variation) is typically 5-10 percent for any lab, while total precision among labs is 10-25 percent. However, in most cases of poorer total precision, the cause is either a systematic bias between two or more labs or inadequate low-level performance by one or more labs. These findings suggest that additional standardization in methodology is warranted.

**INTRODUCTION**

In 1988 EPA's Clean Air Science Advisory Committee recommended<sup>1</sup> that existing measurement methods for acid aerosols be evaluated because acid aerosols were under consideration for possible listing as a seventh criteria pollutant. Most of the existing methods are variations of one basic method in which ammonia gas, which could neutralize acidity collected downstream, is removed by diffusion to an acidic wall; the particles are removed by a Teflon filter and later extracted with a dilute solution of a strong acid and analyzed by a pH electrode. Another method, developed by Brookhaven National Lab, uses no denuder for ammonia, but collects the particles on a quartz filter with later extraction and analysis by Gran titration.

Before beginning the studies it was concluded that the most appropriate indicator of aerosol acidity is fine particle strong acidity measured as hydrogen ion by either pH or titration<sup>2</sup>, and that because no standard for aerosol acidity existed, accuracy could not be established by these studies. EPA then sponsored a series of intercomparisons to judge the relative performance of the methods.

**SINGLE COMPONENT AEROSOLS**

The first study involved three laboratories sampling from a

manifold, which was a 3 m long, 15 cm diameter, Teflon-coated aluminum pipe. None of the samplers used a particle size classifying inlet. All three samplers were of the same basic type (annular denuder to remove ammonia, Teflon filter, and pH determination of acidity). Sulfuric acid aerosol was generated by nebulization first at a low concentration for three sampling periods, and then at a high concentration for three more sampling periods. Each lab operated two samplers for each experiment so that intralaboratory precision could be determined. The same design was then repeated using an ammonium bisulfate aerosol.

There was substantial agreement on acidity among the labs (Figure 1). Each lab's two values for one experiment were often very close, while there was a greater difference between labs. One lab was consistently higher than the median, while another tended to be lower than the median. The intralab precision averaged 5 percent, while the total precision across all labs was 14 percent.

#### **MULTICOMPONENT AEROSOLS**

The second study included the same three participants and the same physical apparatus as the first study, but used more complex test aerosols. First was a test of a procedure to correct for the possible neutralization of acidity on the Teflon filter by ammonium nitrate aerosol, which if present will pass the ammonia denuder as particles and then may dissociate on the Teflon filter to release ammonia. The design was to sample sulfuric acid aerosol and, without disturbing the samplers, change the nebulization solution and sample ammonium nitrate aerosol. Reference samplers which were changed between the two components provided a measurement unbiased by the possible artifact. This test was done in triplicate but at only one level. The second part of this study was to generate an artificial smog by the photochemical reaction of toluene,  $\text{SO}_2$ , and  $\text{NO}_x$ . It was found that not enough acidity was generated by photochemistry alone without going to undesirably high concentrations of  $\text{SO}_2$ , so most of the acidity was added by nebulizing sulfuric acid; nevertheless, there were possible confounding species present in the aerosol, including ozone and organic acids. These smog experiments were done in triplicate at each of two concentrations.

The overall results for these experiments showed that, although most intralab precisions were similar to those of the single component aerosols, there was about twice as much total variability (Figure 2). This seemed to be due to a systematic bias of 30-50 percent between one lab and the other two. In the  $\text{H}_2\text{SO}_4/\text{NH}_4\text{NO}_3$  experiments, only about 25 percent of the acidity was found on the Teflon filter; therefore, the correction was an important factor. Two of the labs came very close to the reference values. Thus, in this test the correction scheme appears to work well.

#### **OUTDOOR SMOG CHAMBER STUDY<sup>3</sup>**

Six laboratories, including five that used the basic method and one that used the Brookhaven method, participated in the chamber study held at the University of North Carolina's 190 m<sup>3</sup> outdoor smog chamber. Two experiments of each of the following types were conducted: sulfuric acid only, photochemical smog with added sulfuric

acid, photochemical smog with added sulfuric acid and dust, and dust followed by photochemical smog with added sulfuric acid. Again, each group ran two samplers in each experiment. Nebulized sulfuric acid was added in every photochemical experiment due to the inability of the photochemistry to generate enough acidity. For the experiments using dust, General Motors fine natural Arizona dust was generated by a venturi-based deagglomeration system.

Intralab precision for acidity was about 10 percent. The total precision was 25 percent for all experiments, but reduced to 12 percent for the four highest level experiments. A graph of precision versus concentration displays the behavior typical of most analytical methods (Figure 3) and implies that a minimum loading of about 700 nanomoles  $H^+$  is needed to avoid the level below which interlaboratory variance increases dramatically.

#### **EXTRACTION AND ANALYSIS STUDY<sup>4</sup>**

The final study was undertaken to examine the possible major contributors to imprecision, including extraction and analytical performance, and to examine the methods' performance on real versus synthetic samples. By having one group collect the atmospheric samples, factors such as flow rate and sampler differences could be eliminated as sources of bias. The first test was of spiked filters in triplicate at six different concentration levels; each lab had to extract and analyze its filters. The second test was of atmospheric samples collected by one laboratory; two or more filters for three sampling periods were extracted and analyzed by each lab. The third test was of atmospheric samples that were all extracted by one lab, with the resulting extract solutions for each day combined, spiked, and divided among the labs for analysis.

Intralab precision was found to be 5 percent, while total precision was about 10 percent. The lowest level of spiked filters shows a large variation among labs, whereas the second and others do not (Figure 4). This implies that with the current level of performance, one should try to collect at least 400 nanomoles  $H^+$  in order to get good comparability among labs. The ambient filters all show good interlab precision, indeed somewhat better than the spiked filters. This implies that analysis of real atmospheric samples is no less precise than that of spiked samples. Thus, spiked filters can be used in conducting quality assurance on an acid aerosol measurement network. The extract solutions have good interlab precision also, marginally better than the spiked or ambient samples. This indicates that there is a identifiable but not major effect of extraction by the different labs.

#### **CONCLUSIONS**

1. Intralaboratory precision expressed as the coefficient of variation was typically found to be 5-10 percent. The total precision, which includes both intra- and interlaboratory sources, typically ranged from 10-25 percent. The higher cases were usually associated with systematic bias or inadequate low level performance affecting one or two groups. These differences would probably be reduced by the adoption of a common sampling and analysis protocol, such as the one the U.S. EPA has recently published<sup>5</sup>.

2. No statement can be made about the accuracy of the methods for acidity owing to the lack of an accepted standard. Thus, since all methods generally showed good internal precision, one method of measuring aerosol acidity cannot be recommended over another.
3. The correction scheme for on-filter neutralization by ammonium nitrate worked well under the experimental conditions used.
4. Atmospheric acidity samples have a comparable precision to spiked samples. This supports the use of spiked filters for quality assurance of acid aerosol measurement networks.
5. Networks involving different groups should design their sampling strategy (flow rate and sampling period) so that at least 400-700 nanomoles of H<sup>+</sup> are collected at the desired minimum detection limit for the network.

#### DISCLAIMER

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. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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5. Determination of the Strong Acidity of Atmospheric Fine-Particles (<2.5 μm) using Annular Denuder Technology, EPA/600/R-93/037, U. S. Environmental Protection Agency, Research Triangle Park, NC, 1992.

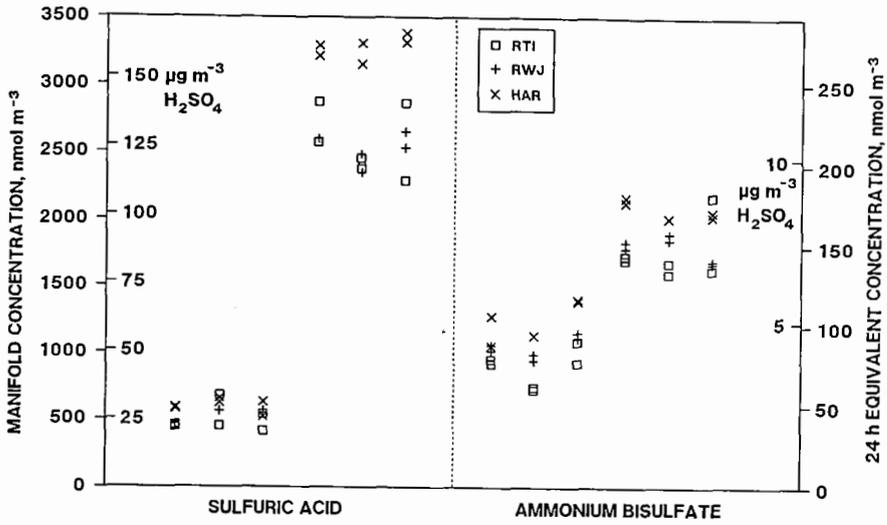


Figure 1. Acidities for single component aerosols.

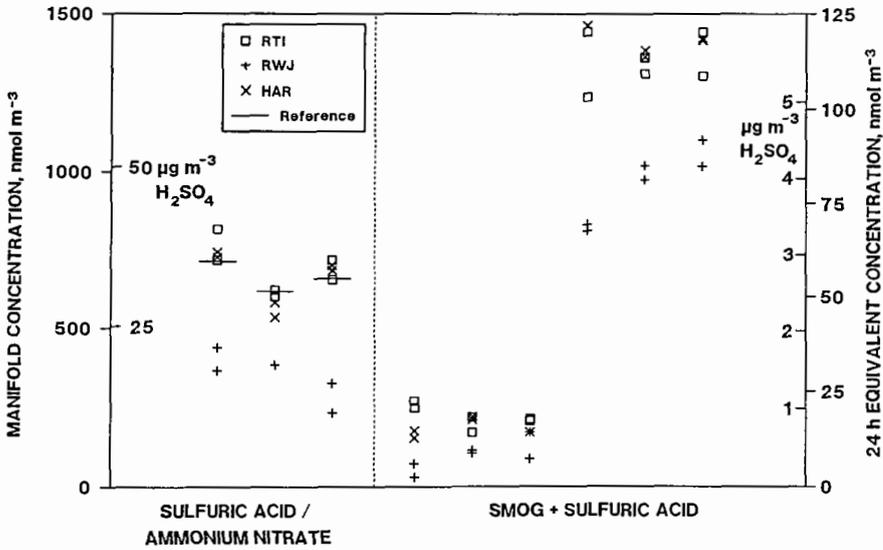


Figure 2. Acidities for multicomponent aerosols.

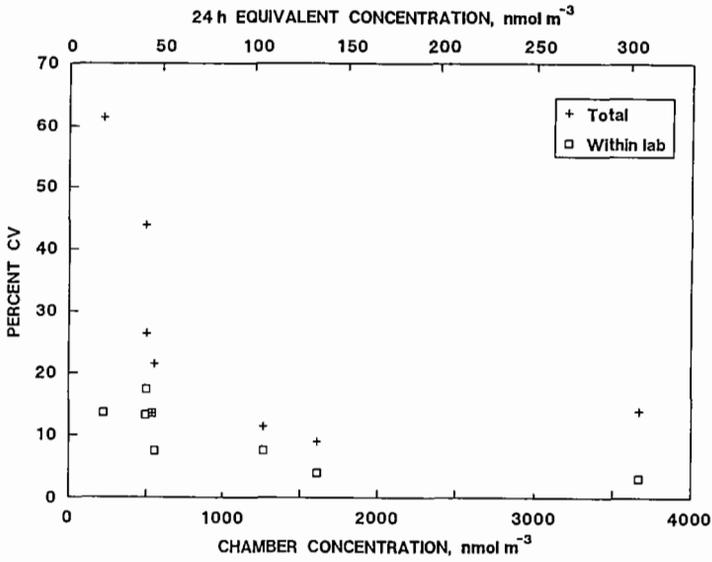


Figure 3. Coefficient of variation versus level in the outdoor chamber study.

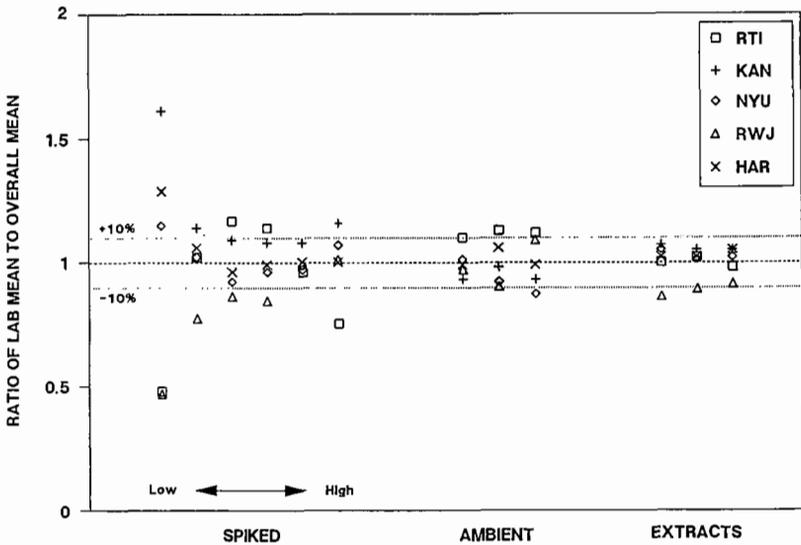


Figure 4. Lab means compared to overall means in the extraction and analysis study.

## Speciation and Determination of N-Nitrosodimethylamine and NO<sub>x</sub> Species in Ambient Air by Surface Specific Preconcentration

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### ABSTRACT

Recently there has been an increased interest in the quality of indoor air and its components. Of particular concern are volatile compounds which are either known or potential carcinogens, such as the nitrosamines. A method has been developed to speciate and quantify N-Nitrosodimethylamine in the presence of other NO<sub>x</sub> compounds. Volatile nitrogen compounds are separated and preconcentrated on a sequential series of specially coated hollow tubes. Sample analyses are achieved by sequential thermal desorption followed by conversion of absorbed analytes to NO which is then detected by a reduced pressure chemiluminescence analyzer. Detector response is linear with sample size and the current detection limit is approximately 0.25 ng/sample or 0.05 ng/L for a typical ambient air sample. Preliminary ambient air analysis indicates the presence of N-Nitrosodimethylamine in concentrations in the fractional to low nanograms/L range which is consistent with results published using other methods.

### INTRODUCTION

Concern regarding the indoor environment has been on the increase. Toxic chemicals have been monitored and acceptable levels have been determined for some. The family of NO<sub>x</sub> compounds has been extensively studied and monitored and recently concern has arisen over exposure to high levels of the volatile nitrosamines. Many nitrosamines have been studied for years and many have been found to be carcinogenic. Without further investigation into the ambient concentrations of these compounds, it would not be possible to determine an acceptable level for the volatile nitrosamines, such as, dimethylnitrosamine, diethylnitrosamine, methyl-ethylnitrosamine, and nitrosomorpholine.<sup>1</sup> Nitrosamines form in air when both NO<sub>x</sub> and secondary and/or tertiary amines are present. Rapid formation is favored in dark and in humid conditions. Formation also occurs during the daytime, however molecular photolysis occurs. Many groups have observed half-lives for the volatile nitrosamines on the order of 30 minutes in sunlight and 60 minutes on a cloudy day.<sup>2,3,4</sup> Investigation into indoor half-lives has not been documented.

The existing methodologies for nitrosamines utilize mostly GC, MS, GC-MS, HPLC, TEA (chemiluminescence), or a combination.<sup>5,6,7,8</sup> The current literature lists TEA as having the most accurate detection and the highest recovery of the instrumental techniques. The most reported sample collection technique involves sampling air and collecting on a sorbent, such as carbon, Tenax, or a Thermosorb cartridge.<sup>9</sup> After collection freeze trapping, elution, concentration, and/or reduction are often involved. The published methods also only identify the nitrosamine, and do not give any information on additional NO<sub>x</sub> species. The current methods, while they have good sensitivity and reproducibility, are time consuming, labor intensive, and costly. Analysis procedures that monitor more than one NO<sub>x</sub> species, and that are quicker, easier, and less expensive would be beneficial.

Braman and coworkers have previously reported on the application of coated hollow tubes for the preconcentration and collection of volatile species, both NO<sub>x</sub> and organics.<sup>10,11</sup> They have

monitored  $\text{HNO}_3$ ,  $\text{HNO}_2$ ,  $\text{NO}_2$ ,  $\text{NH}_3$ ,  $\text{NO}_2$ , and  $\text{NO}$  simultaneously. Cobb et al. used coated hollow tubes for the analysis of specific atmospheric organics. The development of a more viable technique for nitrosoamine monitoring is needed. Without additional information and data profiles of the indoor environment, control and/or removal of a potentially carcinogenic source would not be possible. The focus of this study was to develop the appropriate combination of tubes and to employ them for the determination of specific  $\text{NO}_x$  species, as well as, volatile nitrosamines in indoor air. The hollow tube technique allows for quick  $\text{NO}_x$  speciation, and analysis, as well as avoid the drawbacks of nitrosamine degradation and artifact formation.<sup>9,12</sup>

## EXPERIMENTAL

### Instrumental

A Thermo Electron Model 14B/E chemiluminescence analyzer was used and operated in the manual mode. The automatic functions were disabled and all compounds under analysis were converted to  $\text{NO}$  previous to entering the instrument. Calibration of the detector response was done using either standard calibration gases and/or for the nitrosamines, a permeation tube gas standard. The critical instrumental parameters were sample chamber vacuum of 25 torr, He carrier gas flow of 100 ml/min, and an inboard flow of 75 ml/min. With these flow rates the detection limit was 0.006 nanograms as N with a reproducibility of sample response of  $\pm 95\%$ .

### Tube Preparation

All chemicals used in the tube preparation were reagent grade and all tubes were made of 6 mm O.D. X 30 cm. quartz. Each tube was etched 5 min. in a 50% HF solution, rinsed, then boiled in 40% NaOH. After the surface prep. the tubes were rinsed and boiled in DI for 1 hr, rinsed and stored under DI until needed for coating. Previous to coating the tube was oven dried and cooled. Without a through surface prep., coatings did not adhere well, blank properly, function correctly, or last long.

Iron oxide coating. An iron hydroxide gel was made using  $\text{FeCl}_3$  or  $\text{Fe}(\text{NO}_3)_3$  and NaOH and the mixture was drawn through the tube to give an even wetting of the interior surface. The tube was dried with He carrier gas flowing through. After drying the tube was heated to approx. 500 °C with  $\text{O}_2$  passing through. This process expelled both  $\text{Cl}_2$  and and/or  $\text{NO}_x$  and a orange-red crystalline iron oxide coating was formed.

Copper iodide coating. Copper iodide coated tubes were prepared by making a slurry of CuI from CuCl and KI and pulling this mixture through the tube. The tube was first dried then heated to 300 - 400 °C, while passing He gas. During the heating some sublimation of  $\text{I}_2$  may be observed. The resulting tube has a brittle, translucent tan-white coating.

Carbon and acid doped carbon coatings. Carbon tubes were made by pulling smoke from a benzene fire through the tube until no bare patches were noticed on the tube walls. For acid doping, a 1:1 mixture of  $\text{H}_3\text{PO}_4/\text{H}_2\text{PO}_4^-$  was quickly pulled through the tube, wetting the carbon surface, but not removing it. He carrier gas is again used for drying and blanking at 400 - 500 °C. The heating was done until no more oil-like residue was observed.

Cobalt oxide coating. Tubes coated with cobalt oxide were made by either using a saturated  $\text{Co}(\text{NO}_3)_2$  or by making a cobalt hydroxide gel from  $\text{Co}(\text{NO}_3)_2$  and NaOH. As before, the tube was dried with He and after setting the surface the tube was heated to 500 °C with  $\text{O}_2$  passing through. The resulting coating was a glassy blue-black.

**Conditioning.** All tubes required significant conditioning before reproducibility and correct compound discrimination was observed. After blanking, gas standard samples were cycled on and off each tube. If tubes had a variance of >5% in their reproducibility, the tube was rejected, cleaned, and recoated. The cycling was necessary to set the active surface. The surfaces used are thought to be Fe<sub>2</sub>O<sub>3</sub>, CuI, amorphous carbon, and Co<sub>2</sub>O<sub>3</sub>. These surfaces, as well as some others, are presently under further investigation and improvement.

#### Standards

A permeation tube gas standard for Nitrosodimethylamine, NDMA, was assembled. The source consisted of a 30 °C water bath with liquid NDMA in a stainless holder with a teflon diaphragm. A diffusion hole was located in the diaphragm and source was placed in an additional holder and submersed. Air was flowing through approximately 25 ft. of tubing before the standard to ensure a constant temperature. The air flow rate over the standard is > 8 L/min and sampling was done using a "T" port between 0.5 - 1.0 L/min. The source response was checked versus standard calibration gases of NO and NO<sub>2</sub>, and was in good agreement. The source output was 35.63 +/- 3.76 ng/min as total N for over 8 months. The source for HNO<sub>2</sub> has previously been described by Braman et al.<sup>13</sup>

#### Air Sampling

Air, both indoor and outdoor, was sampled using a small air pump, that had a previously calibrated rotometer attached. The flow rate during sampling was between 0.5 - 1 L/min with the total volume to be analyzed at < 10L. This allowed for duplicate samples and for indoor sampling, limited inconvenience to the businesses being sampled. The tubes were connected with teflon connectors and in the order of iron oxide, copper(I) iodide, carbon (or H<sup>+</sup> doped carbon), and cobalt oxide. For transport the tubes were disassembled and capped.

#### Analysis

Each tube was analyzed individually using thermal desorption with either a quartz, gold coated quartz, or no catalyst bed. The catalyst bed temperature ranged between 300 - 500 °C depending on the output desired. In line after the cat. bed was a H<sub>2</sub>O bubbler followed by an empty bubbler and air make-up "T". Each individual tube required less than 10 minutes to completely analyze and reblank and prepare for the next sample.

## RESULTS AND DISCUSSION

#### Individual Tube Response

The copper(I) iodide and cobalt(III) oxide tubes have been characterized in previous work.<sup>10</sup> The copper(I) oxide tube collects HNO<sub>3</sub>, HNO<sub>2</sub>, and NO<sub>2</sub> and in addition to these compounds the cobalt(III) oxide tube collects NO. The collection of both volatile nitrosamines and amines has not yet been examined, however collection of these compounds is expected. For this study, instead of using the mixed potassium-iron oxide tube developed by Cantera<sup>10</sup>, an iron oxide tube was substituted. This tube collected HNO<sub>3</sub>, HNO<sub>2</sub>, and trace amounts of NO<sub>2</sub>. The response was in agreement with the mixed oxide tube, however the conditioning and blanking procedure were far superior to the other tube. It is thought that there is a combination of chemi and physisorption occurring on the coated tube surface. The conditioning of the tube most likely either causes a charge migration of an active species, and/or causes the surface to crack and develop the topography necessary to hold the analyte molecules. Determination of the active species and examination of all of the tube surfaces is presently under way.

From previous work,<sup>10</sup> the catalyst of choice, used in the analysis stream, was gold. For most of the collection surfaces, a catalyst bed was necessary to ensure complete conversion of the thermally desorbed species to NO. The gold surface provided adequate reduction sites for the NO<sub>x</sub>, however, it appeared to be a collector of particulate and organics. The output from this cat. bed led to peak tailing. When using this catalyst, the surface buildup prohibited a clean release of the molecules of interest. For this study, superior, cleaner results were achieved using a 15 cm heated quartz tube. The response using quartz gave sharper peaks with a quick return to the baseline. It is thought that the quartz surface is smoother and has enough active sites for any needed decomposition of NO<sub>x</sub> analytes to NO. All tubes were tested with each surface and with standards. The comparison between the two types of heated catalyst tubes yielded comparable results.

Both types of carbon coated tubes were found to collect all of the before mentioned NO<sub>x</sub> species, except NO, as well as the volatile nitrosamines and volatile amines. Using the permeation tube NDMA standard, the carbon and H<sup>+</sup> doped carbon tubes(H-C) were characterized. The capacity determined previously by Cobb<sup>11</sup> was > 500 ng for atmospheric organics. The base capacity for NDMA, and volatile nitrosamines has not been tested yet, due to the fact that the size of the samples and amounts recorded for this species are at least one order of magnitude lower. By employing a dual tube analysis, the scrubbing efficiency for NDMA, for both types of carbon tubes, was found to be 93.00 +/- 2.54 % in the low ng/L range. Based on the Gormley-Kennedy equation<sup>14</sup>, which predicts the efficiency of hollow tubes used for chemisorptive preconcentration, a calculated value of 94.6 % was found. The experimental and predicted values were within the standard deviation, and in good agreement. Testing was done to determine the decomposition lifetime of NDMA when absorbed onto both the C and H-C surface. No detectable change was observed after 20 hours of storage, however by 66 hours of storage a 5 % loss was noticed.

Catalyst testing. Scavenger solutions and catalyst bed effects were also examined . It has previously been determined that the weakest bond is the N-N bond that releases the nitrosyl portion of the molecule. Experiments were run to determine if upon thermal desorption and testing whether the nitrosyl portion and/or the amine portion were converted quantitatively to NO. Using the published scavenger solution<sup>15</sup> method for analyzing nitrosamines in solution, a loss of standard was observed, and only 81 - 87 % of the NO was detected. It was found that if the catalyst bed were omitted, upon thermal desorption from the C or H-C surface, 95 % of the NO group was detected. Using a heated quartz bed, 98 % of the NO group was observed. If a gold coated bed was used, not only was response recorded for the NO group, but also for the amine portion. In the low ng/L, it was determined that 98 - 99 % of the total N was detected. Also, testing of volatile organic amines, it was found that upon desorption, and only if the gold catalyst bed was used, NO was produced quantitatively.

Comparison between the C and H-C tube response for NDMA showed that the C tube desorbed the amine portion, or amines at a slightly lower temperature then the HC tube. This would imply an acid/base type attraction between the amine/amine portion of the analytes and the tube coating. With the H-C tube and gold catalyst bed, two unresolved peaks are often observed for the NDMA molecule. This would also support two types of surface attractions. Attempts to resolve and quantify these peaks are still underway. The reproducibility on both carbon surfaces was < +/- 5 %, in the low ng sample size. The 5 % criteria was the limit for initial tube rejection, so the deviation observed in reproducibility may due mostly to tube manufacture. The estimated detection limit for NDMA using the C and H-C tubes was found to be 0.0064 ng as N. Based on the cat. bed response, tandem air samples are run at each location. The H-C tube from each stack was analyzed using a quartz tube catalyst, which gave only an NO response from the volatile

nitrosamines. The carbon tube was analyzed with a gold tube catalyst, and both portions of the nitrosamine as well as any amine responded. By difference, the level for total nitrosamines and total amines can be determined.

#### Air Analysis

Indoor air profiles are presently being done at this laboratory. Central Florida homes and businesses are being tested. Sampling is done both indoor and outdoor at all locations because many Florida buildings are not tight. In the cooler months, many building are open, and air flow is due to windows and fans, not heating and A/C. The preliminary findings, located in Table I, show levels of NO<sub>x</sub> and volatile nitrosamines similar to previously published data. Of the locations tested, indoor and outdoor profiles are also similar, as expected. One area expected to be high in amines, medical facility, kennel, gave high amine results. This high amine area was an example of the analysis technique for species separation using the carbon tubes.

**Table I:** Indoor and outdoor air results for NO<sub>x</sub>, volatile nitrosamines, and organic amines. Four tube system, reported as ng/L

		Phosphate Plant A		Medical Facility A	
		3/09/93 <sup>a</sup>	3/23/93 <sup>b</sup>	4/08/93 <sup>c</sup>	
HNO <sub>2</sub>	lab <sup>1</sup>	3.765 +/- 0.817	6.124 +/- 1.949	surgery	14.98 +/- 1.195
	med. <sup>2</sup>	2.840 +/- 0.773		kennel	9.552 +/- 1.072
	out. <sup>3</sup>	3.326 +/- 0.142		outside	13.91 +/- 2.022
NO <sub>2</sub>	lab	8.562 +/- 0.555	7.415 +/- 2.459	surgery	57.33 +/- 10.64
	med.	9.561 +/- 5.195		kennel	36.85 +/- 5.141
	out.	6.903 +/- 1.568		outside	41.81 +/- 3.950
NO	lab	5.198 +/- 1.422	2.284 +/- 1.021	surgery	15.57 +/- 0.586
	med.	4.554 +/- 1.011		kennel	31.08 +/- 2.602
	out.	2.528 +/- 0.453		outside	10.89 +/- 1.734
N (total N in R <sub>2</sub> N <sub>2</sub> O)	lab	1.193 +/- 0.078	1.682 +/- 0.584	surgery	3.367 +/- 0.038
	med.	0.791 +/- 0.041		kennel	11.30 +/- 0.126
	out.	0.864 +/- 0.057		outside	4.526 +/- 0.051
N (total N in amines)	lab	<0.001	1.485 +/- 0.445	surgery	<0.001
	med.	8.100 +/- 0.534		kennel	12.63 +/- 0.141
	out.	<0.001		outside	0.210 +/- 0.002

1 - Q/C wet chemistry laboratory

2 - in house medical facility

3 - outside

a - sunny, breezy day in the 70's, A/C on

b - sunny, high 70's, no A/C in buildings

c - partial clouds, high 70's, A/C on

## CONCLUSION

The use of sequential hollow tube set of iron oxide, copper(I) oxide, carbon or acid doped carbon, cobalt(III) oxide, has been used to successfully collect and concentrate ambient air species of NO<sub>x</sub>, volatile nitrosamines, and organic amines. This tube set, in conjunction with an optimized chemiluminescence detector, gives an accurate profile of the examined species. This analysis scheme circumvents the time consuming sample collection, preparation, and analysis, of other methods. Determination of the ambient nitrosamine concentration is necessary to determine baseline levels, as well as, defining acceptable levels. This technique has the potential for monitoring both indoor and outdoor air in the low ng/L level.

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## MEASUREMENT OF AMBIENT PARTICLE PHASE ORGANIC ACIDITY USING AN ANNULAR DENUDER-FILTER PACK SYSTEM

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### ABSTRACT

Little is known about the extent to which organic acids contribute to aerosol acidity. This paper presents the results of a field study to determine the particle phase concentrations of organic acids using an annular denuder-filter pack system.

Filter samples were cut in half and analyzed first by pH meter to determine strong and total weak acidity. Samples were titrated to beyond pH 9, and total strong and total weak acidity were determined by modified Gran plot. Particle phase strong acidity was found to range from ND to 398 nmole/m<sup>3</sup>. Particle phase total weak acidity was found to range from ND to 167 nmole/m<sup>3</sup>. The concentrations of aerosol strong and weak acidity were found to be highly correlated over the study period ( $R^2=0.93$ ,  $p < 0.001$ ).

### INTRODUCTION

The concentration of ambient particulate matter increases during photochemical smog episodes. Analysis of the organic photochemical aerosols sampled during smog episodes has identified the presence of carboxylic acids (1-16) and dicarboxylic acids (8, 12-14, 16-23). Mono- and di-carboxylic acids have also been identified in ambient particulate matter sampled at rural area receptor sites for regional photochemical pollution from the Ohio River Valley (24, 25). Monocarboxylic acids have been found ambient aerosols sampled in residential areas (26), rural areas (5, 27), and remote areas (2, 28, 29).

Carboxylic acids of twelve or more carbons are commonly found in the particulate phase. The pure compound vapor pressures of C<sub>14</sub>-C<sub>18</sub> acids and C<sub>5</sub>-C<sub>6</sub> diacids are low enough that they should be found exclusively in particulate phase at ambient temperatures (30). Organic acids up to C<sub>10</sub> have been found in gas samples (31), and organic acids C<sub>10</sub> and larger have been identified in particulate matter (12). The only dicarboxylic acid found in gas samples has been oxalic acid, reported in several studies (17, 32). Dicarboxylic acids up to C<sub>16</sub> have been identified in ambient aerosol samples (14).

Data are limited, but organic acids seem to account for as much as 18-20% of the organic fraction of ambient aerosols in urban areas during photochemical smog episodes (1, 5, 15). Smog chamber studies (33-37) have investigated the formation and growth of aerosols from atmospheric organic systems (with NO<sub>x</sub> and/or O<sub>3</sub>), and found that some classes of organic compounds form aerosols quite efficiently. Diolefins and cycloalkenes, in particular, are potent organic aerosol precursors (33-35, 38). The major components of organic aerosols formed in smog chambers from diolefins and cyclic olefins have been found to be dicarboxylic acids and oxo-carboxylic acids.

There are several known and suggested primary sources of ambient particulate phase organic acids. Biogenic sources of ambient particulate phase long-chain carboxylic acids include vascular plant waxes and microbes associated with plant lipids (10-12, 15, 28), the microbiota of marine and lacustrine environments (12, 15) and soil (6). Long chain organic acids are also emitted directly by operations involving animal fats and soaps (18), in substantial quantities by charbroiling and frying of meats (39), and by the combustion of organic materials (6, 12, 40).

Long chain carboxylic acids have several suggested secondary sources. The most generally accepted (37, 38, 41, 42) is the ozone oxidation of olefins, forming Criegee biradicals which isomerize to form an acid. A source of the long chain olefin has been suggested to be plant lipid material (10, 28, 33, 43). Another suggested source of long chain carboxylic acids is the ozone

oxidation of aldehydes, via a Criegee intermediate (37).

Dicarboxylic acids have fewer primary sources. The major primary source has been determined to be motor vehicle exhaust (17, 44). Significant amounts of dicarboxylic acids are also emitted by charbroiling of meat (39). Plants and soil are not important sources of ambient particulate dicarboxylic acids (17).

It has been reported that dicarboxylic acids are found almost exclusively in submicron particles (23), suggesting a photochemical origin. Submicron aerosols are strongly associated with secondary origin, especially for carbonyl and dicarbonyl compounds (34, 38, 44). Several studies (18, 21, 22) have observed strong diurnal variation of particulate phase dicarboxylic acids during long range transport of photochemical pollution from urban areas, well correlated with the ozone concentration, which also supports a photochemical origin.

There are several proposed mechanisms for the in situ formation of dicarboxylic acids. Norton, et al. (32) measured oxalic acid in both gas and particulate phase in Colorado air. They suggested the most likely source would probably be the gas or aqueous phase oxidation of glyoxal (CHOCHO) by hydroxy radical. Other possible secondary sources of dicarboxylic acids include the ozone oxidation of unsaturated fatty acids emitted from vascular plant waxes (10, 14, 43) and soils (14), and the oxidation of diolefins (18, 34, 35).

The oxidation of cyclic alkenes by ozone (or by hydroxyl radical) is a widely accepted secondary source of dicarboxylic acids (18, 21, 22, 34-36, 45). The reaction proceeds with ozone addition across the double bond, followed by ring opening. The product of the reaction is a difunctional molecule, with an aldehyde end, and a Criegee biradical at the other end. The biradical isomerizes to carboxylic acid, and the aldehyde is then further oxidized to an acid group.

The major source for particulate phase organic diacids has been shown to be photochemical formation (22), accounting for up to 70% of the particulate diacids. The long chain fatty acids, however, display a strong even-to-odd carbon preference in ambient particulate matter, clearly indicating their biogenic origin (10, 43). The importance of aerosol weak acidity is still uncertain. Few measurements of aerosol weak acidity have been made. Little is known about the contribution of organic acids to aerosol acidity. Ferek, et al. (25) found that weak acidity comprises approximately 26% ( $\pm 12$ ) of the aerosol total acidity in rural area receptor sites for photochemical pollution from the Ohio River Valley. They analyzed the samples by ion chromatography (for low molecular weight dicarboxylic acids) and found that dicarboxylic acids of six or fewer carbons accounted for 33-127% of the aerosol weak acidity.

Human health effects of particulate weak (or organic) acidity have not been investigated; there is no evidence that carboxylic acids or dicarboxylic acids are mutagenic (46) and no known chronic toxicity associated with a long term low level exposure (47). The primary interests in studying particulate organic acids have included exploring their visibility effects (1) and understanding their tropospheric chemistry.

## MEASUREMENT OF TOTAL STRONG AND TOTAL WEAK ACIDITY

Theoretically, if there is only one acid present, and its dissociation constant is known, the concentration of the acid can be determined from the pH of the acidic solution by a simple calculation. Practically, however, the accuracy of this method is not very satisfactory (48). When more than one acid is present or the  $K_a$  of the acid is unknown, titration is necessary to determine concentration.

The potentiometric titration of a weak acid with a strong base can be difficult; the inflection point of the pH v. titrant added curve can become hard to identify. Further, it has been shown that, for sufficiently weak acids, the inflection point does not correspond well with the equivalence volume (49). The most commonly used method to determine the equivalence point in potentiometric titration is probably the Gran plot (50) or a modified form of the Gran plot. The

Gran plot is a graphical linear extrapolation method, which performs excellently when used in the titration of a moderately weak acid with a strong base (51).

The Gran plot is difficult to apply to titration of weak acids because Gran's approximations result in curvature near the equivalence point of very weak acids, as well as at the low pH end of the titration of a moderately strong acid (48, 51-53). To deal with the curvature, Johansson (48) modified Gran's equations and developed a similar graphical (but still approximate) method that greatly reduces the curvature in these cases. The advantage of Johansson's modified Gran plot is that it can be used with mixtures of strong and weak acids, and it has been used successfully in other studies (25, 54).

#### PHILADELPHIA FIELD STUDY

Philadelphia is a large metropolitan area, located in the middle of the northeastern seacoast. During the summer months, the city's air quality is affected by regional photochemical pollution.

The Philadelphia Aerosol Acidity Characterization Study (PAACS) is the first year/ first city of a multi-year Metropolitan Aerosol Acidity Characterization Study. The program is a joint effort of US EPA Atmospheric Research and Exposure Assessment Laboratories and HSPH Environmental Science and Engineering Program to investigate the formation of and human exposure to acid aerosols and other related pollutants (55). The PAACS is a year-long air pollution monitoring study designed to investigate the spatial variation of acidity, sulfates, ammonia, and mass concentrations in an urban area. During the summer months, intensive monitoring was performed at one site (N/E Airport), and included additional measurement of elemental carbon concentration, meteorological conditions, continuous  $\text{H}_2\text{SO}_4/\text{SO}_4^{2-}$ , particle size distribution (episodic only), aldehydes (episodic only), and organic acids (gas and particulate phase).

Between June 28 and August 28, 1992, day time and night time organic acid samples were collected daily at the N/E Airport site. Day time samples were collected between 12:00 and 18:00 EDT, and night time samples were collected between 18:00 and 12:00 EDT. The organic acid samplers were located 1m above the roof of a trailer, a total of 4m above the ground.

The particulate phase weak acidity during the regular daily sampling was measured using an annular denuder-filter pack system. One KOH coated annular denuder was used to trap gas phase organic acidity, and a citric acid coated annular denuder was used to trap  $\text{NH}_3$ , which would otherwise neutralize particulate phase acidity collected downstream on the filter. The sampler's impactor is designed to remove particles of aerodynamic diameter greater than  $2.1 \mu\text{m}$  at a sampling rate of 10 Lpm, and the filter collects the particles smaller than  $2.1 \mu\text{m}$ . The performance of the KOH coated annular denuder to collect gas phase organic acids has already been described (56).

When returned to the home lab, the filters were cut in half in an ammonia-free hood. Half of the filter was sealed in a glass IC vial and stored in the refrigerator at  $4^\circ \text{C}$  (with  $5 \mu\text{L}$  methylene chloride added to reduce biological activity) until ready for extraction, derivitization, and GC/FID analysis. These analyses will be discussed in a subsequent paper. The other half of the filter was analyzed (same day) for total strong and total weak acidity.

The half filter was wetted with ethanol and extracted under ultrasonic agitation with 1.7 mL of solution ( $9.6 \times 10^{-5} \text{ M KClO}_4$  to reduce  $\text{CO}_2$  solubility,  $0.04 \text{ M KCl}$  to maintain constant ionic strength, and 3.2 % ethanol to increase solubility of organic acids). The vials were sonicated for a total of 15 minutes. The pH meter was calibrated with standards at 4.00 and 7.00. A calibration curve was prepared using a series of 7 analytical standards containing both strong ( $\text{H}_2\text{SO}_4$ ) and weak (a mixture of even-carbon fatty acids  $\text{C}_8\text{-C}_{20}$  and diacids  $\text{C}_2\text{-C}_{10}$ ) acid, covering a range of 0 to  $530 \mu\text{mol H}^+/\text{L}$  in both strong and weak acid. The initial pH of each standard was measured, and the standard was titrated beyond pH 9 with  $10 \mu\text{L}$  additions of  $0.004 \text{ M NaOH}$ . The titration was conducted under a purge of  $\text{CO}_2$ -free air, and using a micro magnetic-stirring vane to reduce the streaming potential of the electrode. Total strong and total weak acid concentrations were determined using a modified Gran plot (48, 50). The strong acid calibration curve generally had

a slope very close to 1.0, an intercept close to zero, and an  $R^2 > 0.995$ . The weak acid calibration curve generally had an intercept close to zero, a slope of 0.75 to 0.80, and an  $R^2 > 0.995$ .

Samples were extracted and analyzed in the same manner. Total strong and total weak acid concentrations were corrected using the standard curve. Blank filters and doped filters were used to provide information about the efficiency of the analytical technique. The filters were doped using mixtures of the same acids used in the calibration curve. The recovery of strong acid from doped filters was found to be >95%, and the recovery of total weak acid from the doped filters was found to be >80%. A plot of the calculated values for total strong and total weak acidity against their known values yields intercepts close to 0 (0.000002 for strong acid and 0.00013 for weak acid) and slopes relatively close to 1 (1.096 for strong acid, and 0.799 for weak acid); the measured values are well correlated with their known concentrations ( $R_2$  values of 0.997 and 0.996 for strong and weak acids, respectively).

## RESULTS OF THE PHILADELPHIA FIELD STUDY

Figure 1 contains the concentrations of total strong aerosol acidity measured in Philadelphia. The daytime strong acid concentration ranged from ND to 398 nmol  $H^+ / m^3$ , and averaged 38 ( $\pm 53$ ). The nighttime concentration ranged from ND to 63 nmol  $H^+ / m^3$ , and averaged 19 ( $\pm 14$ ). The overall average was 38 ( $\pm 53$ ) nmol  $H^+ / m^3$ . The day-to-night difference in aerosol strong acidity concentration was found to be significant ( $p = 0.048$ ) by a paired sample t-test.

Figure 1 shows the concentrations of total weak aerosol acidity measured in Philadelphia. The daytime particulate weak acid concentration ranged from 13 to 167 nmol  $H^+ / m^3$ , with an average of 24 ( $\pm 24$ ). The nighttime concentration ranged from ND to 15 nmol  $H^+ / m^3$ , averaging 6 ( $\pm 2$ ). The overall average of the observed concentration was 15 ( $\pm 19$ ). The daytime concentration of particulate weak acidity was found to be significantly higher than the nighttime concentration using a paired sample t-test ( $p < 0.001$ ).

Figure 2 presents the ratio of weak to total aerosol acidity. The daytime ratio was found to range from 0.19 to 0.86, with an average of 0.39 ( $\pm 0.18$ ). The nighttime ratio ranged from 0.18 to 0.84, with an average of 0.30 ( $\pm 0.13$ ). The overall average weak to total acidity ratio was 0.36 ( $\pm 0.19$ ). Weak acidity was found to be a larger proportion of the total acidity during the day than at night. The difference was found to be significant, using a paired sample t-test ( $p < 0.001$ ).

Figure 3 shows the simultaneous day and night concentrations of total strong and total weak aerosol acidity measured in Philadelphia. Total strong and total weak acidity were found to be highly correlated ( $R = 0.93$ ) over the period of the study. Daytime and nighttime concentrations were correlated equally strongly, though the slope of the regression line for the nighttime concentrations is smaller than that for the daytime concentrations.

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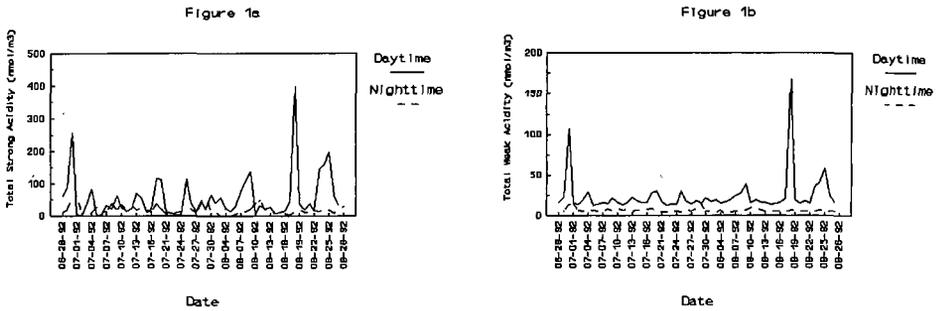


Figure 1 (a) Particulate Total Strong Acidity and (b) Particulate Total Weak Acidity ( $\text{nmol}/\text{m}^3$ ) Measured at the Northeast Airport, Philadelphia, PA, Summer 1992.

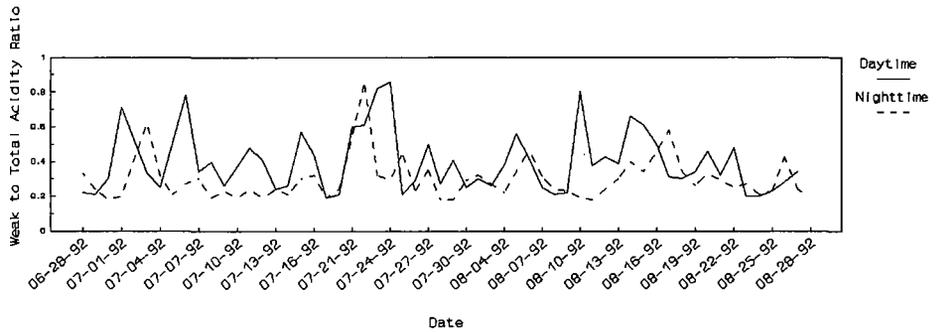


Figure 2 Ratio of Weak to Total Acidity, Philadelphia, PA, Northeast Airport, Summer 1992

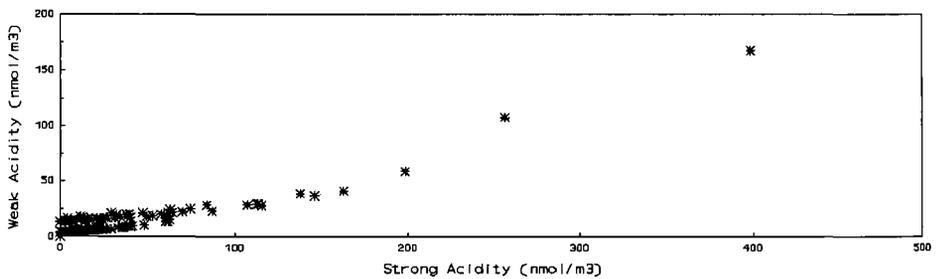


Figure 3 Simultaneous Total Strong and Total Weak Acidity ( $\text{nmol}/\text{m}^3$ ) Measured at Northeast Airport, Philadelphia, PA, Summer 1992. The concentrations are correlated ( $R^2 = 0.93$ ,  $p < 0.001$ ).

*Session 18*

*Indoor Air Quality*

## Ecology of Fungi in Buildings: Relationship to Indoor Air Quality

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### ABSTRACT

In addition to product deterioration, mold growth in buildings can have aesthetic consequences (discoloration, musty odors) and health effects. Effects ranging from fungal pneumonia and pneumonitis to allergies are well documented. We have observed the heavy infestation of register vents and insulation of heating, air conditioning and ventilation systems (HVAC) sometimes without concomitant incidence of fungi in air samples. Studies of the mycoflora of in-duct insulation of an HVAC system demonstrated strains of *Cladosporium herbarum* and *Eurotium herbariorum* that grew on a nutrient medium supplemented with 60% sucrose. Of particular interest was the demonstration of the *in situ* production of ascospores by the *Eurotium* sp. Sexual spores provide the fungus with a resistant stage to survive temperature and moisture fluctuations in the system. Studies of the germination of conidia from several common airborne fungi demonstrated maximal germination on a simple basal medium containing glucose and peptone.

### INTRODUCTION

The presence of mold growth on the internal surfaces of damp dwellings often results in a high airborne fungal spore count which, in turn, presents a distinct health risk to the occupants.<sup>1</sup> In the United States, approximately ten percent of the population suffers from allergies caused by environmental inhalants.<sup>2</sup> Although these allergies tend to be principally of a respiratory nature in atopic individuals, a prevalence of possible toxigenic symptoms including nausea and vomiting, backache, fainting, and nervousness were reported by adults living in damp, moldy dwellings.<sup>3</sup> Common molds (e.g., *Aspergillus*, *Fusarium*, *Penicillium*, and *Stachybotrys* spp.) produce a wide variety of mycotoxins which may cause human diseases.<sup>4</sup> Fungi capable of producing mycotoxins may exacerbate the sick building syndrome.<sup>5</sup> In particular, the establishment of foci of toxigenic fungi and the subsequent release of multitudes of spores represent a serious situation. Moreover, fungal propagules (elements such as spores and mycelia fragments) in high densities in buildings indicate not only a potential health hazard from hypersensitivity and toxigenic reactions but, on some occasions, from infections.<sup>6</sup> An effective mechanism for monitoring indoor fungal burden and the foci of any inoculum is therefore essential.

### Experimental Methods

**Air sampling for microorganisms.** Air samples were collected using a Single Stage Bioaerosol Sampler (Model 10-880, Andersen Samplers, Inc; Atlanta, GA). The Andersen air sampler delivers a constant air sample of one ACFM (actual cubic foot per minute) onto an agar plate. We used five different media (Malt extract agar (MEA), Difco; Corn meal agar (CMA), Difco; Basal media with glycerol (BMGA)<sup>7</sup>; Czapek with 40% sucrose (CZSA), Difco; Sabouraud dextrose agar (SAB), Difco) for 1 minute at each site to maximize the isolation of a variety of fungi.

**HVAC and building material sampling.** Where feasible, the materials were removed as samples. Materials collected were placed directly in sterile sampling bags and returned to the laboratory. Portions of this material were examined directly by white light and Nomarsky microscopy, and other portions stained with fluophores (i.e., acridine orange, fungifluor, Congo red) and examined at appropriate wavelengths. Smaller portions of the material were inoculated into

a variety of liquid fungal growth media to culture the viable components of the fungal community. Portions of the sampled material were examined using the scanning electron microscope.

Where it was not feasible to retrieve material directly but there was some access to the material, we used a modification of the pressure tape method.<sup>8</sup> Acetate film tape (Scotch Brand Acetate Film Tape, No. 800, 3M Company), adhesive side down, was pressed lightly across the surface of the suspect material. The adhesive tape with attached fungal structures was placed directly on a labeled slide at the site. These tape mounts were returned to the laboratory in specialized containers to prevent disruption of the sample. In the laboratory, the tape was removed partially and a drop of lactophenol cotton blue or other stain was placed on the slide. The tape was then pressed back over the stain. These semi-permanent mounts are sufficient for both whitelight, phase contrast, and Nomarsky microscopy.

**Culture maintenance and identification.** Following initial isolation, all dominant fungi (> 20% occurrence) were identified by conventional techniques. Minor isolates (< 20% occurrence) were maintained in pure cultures but were not identified. Cultures were maintained on slant of CMA in screw capped tubes (13 X 100 mm), stored at 5C and transferred at six month intervals during the course of the study. Fungal colonies on enumeration media were subcultured to SAB to assure purity. To reduce contamination by rapid spreading at this stage, we incubated all plates at low temperature (18C) and transferred to final stock culture as soon as identification was confirmed. Fungal identification was based on observation of classic morphological characteristics.<sup>9,10,11</sup>

**Germination studies.** Studies of germination with *Aspergillus flavus*, *A. niger*, and *Penicillium* sp. were conducted to evaluate their ability to germinate on 45 selected media. Following germination, the ability of germinated conidia to grow on the media were assayed. Inocula for each of these studies were prepared as follows. Plates of Sabourauds dextrose agar were inoculated from a stock culture. Following growth for 96h at room temperature (approximately 23C) the conidia were harvested by adding a 5ml of sterile saline (0.9%) containing 0.5% tween 80. The saline was agitated gently with a L-shaped glass rod to release the conidia. The conidial suspension was collected in a centrifuge tube from the petri dish with a pipette. The suspension was centrifuged at 2000rpm, supernate decanted and resuspended in an equal volume of tween/saline. This process was repeated 3 times and the washed conidia were suspended to an optical density of 0.6 (10<sup>7</sup> conidia /ml).

A volume (0.1ml) of this conidia suspension was spread on the surface of various media. A 1cm<sup>2</sup> piece of inoculated media was removed with aseptic technique and placed on a prescored (T) microscope slide. Beginning at the intersection of the two lines ten alternate fields were counted at 0, 12, 18, 24 h. The number of germinated and total conidia were tallied for each time. Media examined included Malt Extract agar (MEA), Potato Dextrose agar (PDA), Tween-80 agar (T-80), Sabouraud Dextrose agar (SAB), Mycological agar (MA), Czapek agar (CzA), Corn meal agar (CMA), Water agar (WA), R2A agar (R2A), Basal agar (BMA), Basal agar + 20% glycerol (BMGA).

**Growth.** Conidia suspensions (50 µl) were spotted on plates at three positions. The plates were incubated at room temperature for up to 72h or until a measurable colony. Measurements of the colony diameter were taken periodically. The growth rate in cm/h was calculated for these time periods and the maximum rate was recorded. Media for which germination data was available also were used for the growth studies.

## Results

From 20 buildings, we have taken 375 samples at 75 sites. The most frequently isolated have been *Aspergillus niger*, *Aspergillus versicolor*, *Cladosporium herbarum*, *Geotrichum* sp., *Penicillium citrinum*, *Penicillium hirsutum*, and *Penicillium variotti*. *Aspergillus flavus*, a known aflatoxin producer, and *Aspergillus fumigatus*, a respiratory pathogen, were isolated on 20 occasions. Comparisons of five media for the recovery of fungi from samples illustrated that a basal media as described by Hocking and Pitt<sup>7</sup> most frequently yielded (13/46) the highest numbers (CFU/m<sup>3</sup>). However, the other media all yielded highest numbers on occasion with Czapek + 40% sucrose agar, as expected, yielded the highest number in only a few cases (4/46). The fungi prevalent in air were not always the same as those found colonizing indoor substrates.

Studies of the germination of conidia isolated from air samples gave varying results (Table I). Of 45 media studied for the germination of conidia no single medium consistently gave the highest germination with the three species tested. *Penicillium* sp. gave high levels of germination on all media except water agar. Low levels of germination of *Aspergillus niger* were observed on Czapek agar and Mycological agar. Germination of *Aspergillus flavus* on Sabouraud dextrose agar was also low. Growth studies suggest similar variation between isolates (Table II). *A. flavus* grew best on CzA but also grew well on T80 agar and CMA. In contrast, *A. niger* grew best on MEA and grew well on BMGA and CzA. The *Penicillium* sp. examined in this work grew poorly on most media. In studies of the survival of conidia under atmospheric conditions, species of *Aspergillus* characteristically were recovered in high numbers after 24, 48, and 96 hours. On the other hand, conidia of *Penicillium* species rapidly lost viability following removal of liquid water.

## Discussion

The relative ranking of germination of species examined on the media was Basal medium > Corn meal agar > Malt extract agar > Sabouraud dextrose agar > Mycological > Czapek with 40% sucrose. While growth studies were inconclusive, comparable growth for all three isolates was achieved on SAB. However, field application of this media often resulted in rapid overgrowth. Considerations of both efficiency of germination and growth rates are essential in selecting an appropriate medium.

Indoor air samples and concurrent sampling of HVAC insulation and filter material suggest that these materials contribute to the fungal burden of indoor air under certain conditions. Moreover, the association of high levels of airborne viable fungi and complaints of poor air quality are not always consistent.

## CONCLUSIONS

Correlations between the perceived quality of indoor air and the presence of measurable parameters such as total viable fungi and total fungi, volatile organic compounds, the presence of certain species would be particularly useful in assessing potential indoor air problems. The use of at least two media (Basal media with glycerol and Czapek with sucrose) to obtain a better indication of number and diversity of viable fungi are recommended. Furthermore, particulate counts or numbers of non-viable fungal propagules should be evaluated.

**Table I.** Germination of conidia of *Aspergillus flavus*, *Aspergillus niger* and *Penicillium* sp. on various media formulations.

	<i>A. flavus</i>	<i>A. niger</i>	<i>Penicillium</i> sp.
MEA	96	93	100
PDA	95	100	97
T-80	98	93	100
SAB	73	93	100
MA	99	79	100
CzA	89	24	100
CMA	98	86	100
R2A agar	95	87	100
WA	49	4	51
BMA	100	98	99
BMGA	88	100	97

Values shown are %germination [(number of spores germinating/total number spores) x 100]. Mean of 10 determinations.

**Table II.** Growth *Aspergillus flavus*, *Aspergillus niger*, *Penicillium* sp. on various media formulations.

	<i>A. flavus</i>	<i>A. niger</i>	<i>Penicillium</i> sp.
MEA	.33	.47	.23
PDA	.21	.33	.15
T-80	.44	.30	.29
SAB	.36	.36	.36
MA	.27	.36	.25
CzA	.51	.41	.25
CMA	.39	.35	.25
R2A agar	.18	.33	.21
WA	0.00	0.00	0.00
BMA	.12	.31	.34
BMGA	.18	.43	.28

Values are the mean of three determinations. Growth rate is expressed in cm/h during maximal growth phase.

**Table III.** Foci of fungal colonization in buildings.

Substrate	Predominant Organism
Fiberglass Duct Liner	<i>Aspergillus sydowii</i> , <i>A. flavus</i> , <i>Cladosporium</i> , <i>Euratum</i> , <i>Penicillium</i> spp.
Filter	<i>Euratum</i> , <i>Acremonium</i> , <i>Penicillium</i> spp., <i>Aspergillus</i> spp.
Ceiling Tile	<i>A. niger</i> , <i>Stachybotrys atra</i>
Wallpaper	<i>Penicillium</i> spp., <i>Aspergillus</i> , <i>Cladosporium</i> sp.
Painted HVAC Vents	<i>Cladosporium</i>

## Acknowledgements

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*Session 19*  
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Mixer-Loader and Applicator Exposure of Nitrapyrin  
to Commercial Handlers and Farmers

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ABSTRACT

Commercial handlers who load N-Serve® (nitrapyrin) into anhydrous ammonia tanks and mini shuttle tanks, as well as farmers who apply nitrapyrin to corn using a tool bar were monitored for respiratory and dermal exposure to nitrapyrin using air sampling and dosimeter techniques. Fifteen workers loading bulk N-Serve® into mini shuttle tanks were monitored and found to have an average respiratory exposure of 0.031 mg/kg BW/day of nitrapyrin and an average dermal exposure of 0.011 mg/kg BW/day. Workers who transferred N-Serve® from mini shuttle tanks to anhydrous ammonia tanks showed an average respiratory exposure of 0.018 mg/kg BW/day and an average dermal exposure of 0.094 mg/kg BW/day. Farmers who applied N-Serve® pre or post emergence to corn showed an average respiratory exposure of 0.0010 mg/kg BW/day of nitrapyrin and an average dermal exposure of 0.0037 mg/kg BW/day.

This paper reviews the methodology and results of the study discussed above.

## INTRODUCTION

N-Serve 24® (nitrapyrin<sup>1</sup>) is a soil nitrogen stabilizer which can be applied by pre-plant incorporation TO corn or by a side dressing. N-Serve is applied at a maximum use rate of 1 lb ai/acre, is marketed in bulk, and applied by soil injection with anhydrous ammonia using a tractor-drawn tool bar.

Farm worker exposure, especially to mixer-loaders and applicators who handle agrochemicals, has been studied and reviewed in the literature extensively (1). While considerable data exists concerning exposure to mixer-loaders or applicators applying liquid or powder formulations of agrochemicals using conventional groundboom aerial or airblast equipment, less data are available concerning exposure to loaders and applicators for agrochemicals which are applied with tractor-drawn tool bars.

The Environmental Protection Agency (EPA) requires that exposure data be available for mixer-loaders and applicators of agrochemicals in order to perform risk assessments on individual agrochemicals currently on the market or being developed for market. This study was designed to determine potential respiratory and dermal exposure of commercial loaders and farmers who apply N-Serve to corn, either preplant or as a side-dressing, using a tractor-drawn tool bar. Whole body dosimetry and air sampling methods were used to accomplish these goals.

## MATERIALS AND METHODS

### Chemical Name

Nitrapyrin (2-chloro-6-(trichloromethyl)-pyridine) is the active ingredient of N-Serve 24® soil nitrogen stabilizer. N-Serve 24® is 22.2% nitrapyrin, 2.5% related chlorinated pyridines, and 75.3% inert ingredients.

### Test Sites

It is important to point out that this worker exposure study was run "in situ"; i.e., the N-Serve used for this study was sold to farmers from mini-bulk containers at the loading facility and the study was conducted with these particular loaders and farmers. There were no discreet packages of N-Serve prepared especially for this study since N-Serve application is an intensive, short, seasonal practice and is dispensed from 250-gallon or larger bulk tanks as the farmer needs it.

There were several test sites in Illinois and Ohio involved in this worker exposure study. Sites consisted of 1) dealer loading sites, and 2) farm application sites. N-Serve is first sold to farmers and pumped into anhydrous ammonia tanks at the dealership at which time the anhydrous ammonia tanks are transferred to the farmers's field and attached to a tool bar applicator prior to application of N-Serve 24® soil nitrogen stabilizer by the farmer. Application was generally to pre-tilled, unplanted corn fields. In some instances N-Serve 24® was

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<sup>1</sup> nitrapyrin (2-chloro-6-(trichloromethyl)-pyridine)

applied as a side dressing to corn plants (4"- 6" high) spaced three feet apart. In either case, the same application equipment (tool bar) and techniques were used by the farmer.

#### Description of Application Equipment

The equipment used in this study consisted of a closed cab tractor attached to a tool bar to which the anhydrous ammonia tank containing N-Serve 24® soil nitrogen stabilizer was attached. The tool bar's nozzles were essentially tubes adjacent to leading bars which were used to break the earth just ahead of injection of N-Serve and ammonia through the tubes. The nozzles (tubes) were under a positive pressure of 40-80 psi. The N-Serve was injected directly into the ground at a ground speed of about 6 mph. The boom length varied from 15 to about 42 from farm site to farm site.

#### Test Subjects

There were three types of test subjects in this study: Dealer Mini-Shuttle (bulk) Tank Loaders (designated DMSTL); Dealer Anhydrous Ammonia Tank Loaders (designated DAATL); and Farmer Applicators (designated FLA).

#### Monitoring Devices

Whole Body Dosimeters. Sears union suits worn under clothing.

Cotton Gloves. Light, white industrial gloves were worn under chemically-resistant rubber gloves. Chemically-resistant gloves were removed during exercise of chores other than loading N-Serve 24® soil nitrogen stabilizer or anhydrous ammonia.

Air Pumps. Chromosorb 106 sorbent tubes attached to Flow-Lite™ air pumps were placed on each individual.

#### Description of Sample Handling from Field Through Analysis

Air sampling tubes, whole body dosimeters, and cotton gloves were taken from test subjects and placed in pre-labeled plastic bags. Air sampling tubes were capped at both ends prior to placing in the plastic bags. The bags were sealed, placed in another plastic bag, and placed in coolers. About 20 lbs. of dry ice was added to each cooler and paper placed on top of the dry ice to help prevent dry ice dissipation. A chain-of-custody form was completed for each shipment. The form contained each sample code, the date shipped, and signature of the shipper. The cooler was then sealed with duct tape and shipped overnight or driven directly to PTRL, Inc., 155 Prosperous Place, Lexington, Kentucky.

#### Field Stability Samples

Blank Samples (Negative Controls). One pair of cotton gloves and one whole body dosimeter were taken directly from their protective cover and placed on a table at the test site during the performance of a replicate and left under the environmental conditions of the test site.

Positive Controls. Positive controls (also referred to as field spikes) were prepared as follows: One whole body dosimeter and one pair cotton gloves were taken directly from their protective covers and placed on a table at the test site away from the N-Serve 24® soil nitrogen stabilizer loading or application area and spiked with a predetermined amount of N-Serve 24® obtained from a mini-bulk tank (high spike). Low spikes were from a solution of N-Serve diluted with solvent. The sample was left out for the duration of the replicate.

Chromosorb 106 Air Sampling Tubes (Positive Control). One sorbent tube was fortified using a Hamilton® syringe with a known amount of nitrapyrin from a tank sample of N-Serve 24® soil nitrogen stabilizer from the test site. The N-Serve was spiked onto the sampling end on the tube. The tube was then placed on the table at the test site and left out under the environmental conditions of the test site for the duration of the replicate.

Analytical Methods. Analytical methods for nitrapyrin on Chromosorb 106 air sampling tubes, whole body dosimeters, and cotton gloves involved extraction of the nitrapyrin from each matrix and analysis of the extract by gas chromatography on GC column (J & W 15M DB-1 Megabore, 5.0 µm film).

## RESULTS

### Method Validation

Analytical methods were validated for Chromosorb 106 air tubes, cotton gloves, and whole body dosimeters. Concurrent recoveries of nitrapyrin was run with each sample set. Average concurrent recoveries for all matrices were between 90-99%.

### Storage Stability

Freezer storage stability studies were performed for nitrapyrin on whole body dosimeters, cotton gloves, and Chromosorb 106 air tubes stored under freezer conditions. Nitrapyrin was stable under freezer conditions for all matrices (89%-101% recovery variance over 90 days in the freezer).

### Results of Determination of Respiratory and Dermal Exposure to Commercial Loaders and Farm Applicators of N-Serve 24®

Fifteen replicates of exposure to each type of worker were performed. The results of this study are summarized in Table 1. Dealer Mini Shuttle Tank Loaders (code = DMSTL) experienced an average potential respiratory exposure of 0.031 mg/kg BW/day and an average potential dermal exposure of 0.011 mg/kg BW/day.

Dealer Anhydrous Ammonia Tank Loaders (code = DAATL) experienced an average potential respiratory exposure of 0.018 mg/kg BW/day and an average potential dermal exposure of 0.094 mg/kg BW/day.

Farmers who apply N-Serve® (code = FLA) with a tool bar experienced an average potential respiratory exposure of 0.001 mg/kg BW/day and an average potential dermal exposure of 0.0037 mg/kg BW/day.

## SUMMARY AND CONCLUSIONS

Potential respiratory and dermal nitrapyrin exposure to commercial loaders and farmers was determined for N-Serve at several locations in Illinois and Ohio.

Dealer Mini Shuttle (bulk) Tank Loaders (DMSTL) exhibited an average respiratory exposure of 0.031 mg/kg BW/day and an average dermal exposure of 0.011 mg/kg BW/day.

Dealer Anhydrous Ammonia Tank Loaders (DAATL) exhibited an average respiratory exposure of 0.018 mg/kg BW/day and an average dermal exposure of 0.094 mg/kg BW/day.

Farmers exhibited an average respiratory exposure of 0.001 mg/kg BW/day and an average dermal exposure of 0.0037 mg/kg BW/day.

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Table 1. Summary table.

Worker Type	Average Exposure (mg/kg BW/day)		
	Respiratory	Dermal	Total
Dealer Mini Shuttle Tank Loader (DMSTL)	0.031	0.011	0.042
Dealer Anhydrous Ammonia Tank Loader (DAATL)	0.018	0.094	0.11
Farmer (FLA)	0.0010	0.0037	0.0047

# ANALYTICAL METHOD FOR THE SCREENING OF PESTICIDES AND POLYNUCLEAR AROMATIC HYDROCARBONS FROM HOUSEDUST

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## ABSTRACT

Neutral pesticides, PAHs and cotinine from housedust were analyzed using single extraction, followed by cleanup and finally by GC/MS. Method validation was performed initially using 28 pesticides and 6 PAHs. Later four more PAHs were added to the list. A 2 g housedust sample was Soxhlet extracted for 16 hours using 200 mL of 6% diethyl ether in n-hexane. The extract was reduced to 5 mL and analyzed. Matrix effect was observed in the extract without cleanup. Cleanup through activated alumina showed poor recovery for most of the target analytes. Cleanup through Florisil showed good recoveries. GPC cleanup showed similar results as Florisil. Cotinine was analyzed without cleanup because of its low recovery (10-14%) in all the evaluated cleanup methods. There was no significant difference in results between immediate and 48 hours delayed extraction after spiking the housedust sample. Reproducible results were observed when extraction and analysis were repeated on the same housedust samples after two months. For organochlorine pesticides reproducible results were obtained when analysis was performed by GC/MS and GC/ECD. High levels of p,p'-DDT and dieldrin were observed in dusts from homes with old rugs, which confirmed very slow degradation of some organochlorine pesticides in the indoor environment.

## INTRODUCTION

Pesticides, polynuclear aromatic hydrocarbons (PAH) and tobacco alkaloids are well known carcinogens and potential biohazards, which are present in housedust. Infants and toddlers are more exposed to such pollutants than adults because of their frequent contact with the floor and hand-to-mouth behavior. Dust is reported to be a major source of home exposure to pesticides<sup>1,2</sup> and strong correlations have been found between levels of pesticides in indoor air and housedust.<sup>3</sup> Track-in is reported to be a major source of pesticides and PAHs in housedust<sup>4</sup> and degradation of chlorinated chemicals in the household environment is slow. These findings have elicited a growing interest in the analysis of pesticides from housedust.

Despite these concerns, there is very little literature information on the analysis of pesticides and PAHs from housedust. It is a challenging matrix for the analysis of any target analyte because it contains numerous chemicals, including foods, cosmetics, chemicals used for indoor pest control, tobacco alkaloids and many other chemicals that are carried in from outdoors. Monitoring specific chemicals from such a complex matrix is extremely difficult. This paper reports a method validation for screening of pesticides, PAHs and cotinine (a tobacco alkaloid), analysis results for some real housedusts, and implications from the analysis.

## EXPERIMENTAL

Method validation was performed by spiking 2.0 g of housedust with a series pesticides, polycyclic aromatic hydrocarbons and cotinine as shown in Tables I and II. Levels of target compounds were varied based on their response factors in GC/MS. All the target analyte standards were purchased from Chem Service, West Chester, PA. p-Terphenyl-D14 was used as surrogate standard to monitor the extraction loss. The spiked dust and same amount of unspiked dust (dust-blank) were Soxhlet extracted in 6% diethyl ether in n-hexane for 16 hours. Then each extract was blown down to a final volume of 5.0 mL using turbo evaporator at 30-40°C under nitrogen stream. Each of the extract was then divided into five aliquots and treated as follows:

Aliquot 1 (1 mL): Solvent exchanged to n-hexane and analyzed by GC/MS by the procedure described later.

Aliquot 2 (1 mL): GPC cleanup - The extract was solvent exchanged to dichloromethane (DCM), GPC cleanup was performed by dual column (Water Envirogel GPC columns, pore size is of 500 Å) using EPA method 3640A. The final volume of eluent was reduced to 1 mL and analyzed by GC/MS.

**Aliquot 3 (1 mL): Alumina cleanup** - Column was prepared by taking 1 g ICN alumina B-Super I (ICN Biomedicals) in a 5 mL glass syringe of 0.5" i.d. and conditioned with 10 mL n-hexane. One milliliter of extract was passed through the column and eluted with 10 mL of 10% acetone in n-hexane. The final volume of the eluent was blown down to 1 mL using turbo evaporator under nitrogen stream and analyzed by GC/MS.

**Aliquot 4 (1 mL): Florisil cleanup** - The procedure was the same as described in alumina cleanup with the exception that Florisil (200 mesh, activated Mg-Silicate, Sigma Chemical Co.) was used as column material. This procedure was used to get the results shown in Table I. The procedure was then changed by using 4 mL Florisil in a 10 mL serological disposable pipet of 8.5 mm i.d., conditioning with 10 mL n-hexane, passing 1 mL extract and then eluting with 20 mL of 10% acetone in n-hexane and blowing down to final volume to 1 mL for analysis.

**Aliquot 5 (1 mL):** Kept as reserve.

Table I. Recoveries of neutral pesticides, PAHs and cotinine from housedust.

Compound	QL (ppb)	Spiked (ppb)	% Recovered			
			NCL	AL	GPC	FL
Alachlor	53	2732	122	97	118	116
Aldrin	39	2001	109	101	106	107
Atrazine	39	2001	119	78	112	114
Bendiocarb	59	3002	141	66	122	129
Captan	78	4002	115	71	129	128
Carbaryl	78	4002	144	109	120	123
$\alpha$ -Chlordane	59	3002	113	110	114	121
$\gamma$ -Chlordane	59	3002	117	78	101	93
Chlorothalonil	59	3002	109	103	121	119
Chlorpyrifos	49	2501	123	97	100	100
Dacthal	59	3002	109	99	104	109
p,p'-DDE	39	2001	103	111	124	128
p,p'-DDT	78	4002	126	113	127	130
Diazinon	49	2501	137	36	84	97
Dichlorvos	78	4002	118	60	68	66
Dicofol	160	8004	37	120	132	127
Dieldrin	39	2001	128	74	101	102
Folpet	78	4002	107	109	115	118
Heptachlor	59	3002	126	106	107	114
Hexachlorobenzene	49	2501	120	99	104	108
Lindane	59	3002	113	72	102	105
Malathion	39	2001	145	95	123	122
Methoxychlor	49	2501	131	117	132	126
cis-Permethrin	230	12006	121	114	114	124
trans-Permethrin	230	12006	112	105	104	117
o-Phenylphenol	39	2001	130	55	102	117
Propoxur	39	2001	134	73	116	122
Resmethrin	120	6003	41	26	46	31
Benz(a)anthracene	59	3002	61	58	87	82
Benzo(ghi)perylene	59	3002	109	99	83	111
Benzo(a)pyrene	59	3002	96	102	90	109
Benzo(b)fluoranthene	39	2001	138	117	82	115
Benzo(k)fluoranthene	39	2001	29	85	89	112
Coronene	78	4002	84	84	46	104
(-)-Cotinine	120	3002	101	11	14	14
p-Terphenyl-D14	20	2500	113	108	108	116

Table II. Recoveries of neutral pesticides and PAHs extracted 48 hours after spiking housedust samples.

Compound	Spiked (ppb)	% Recovered	
		HD Sample #1	HD Sample 26
Alachlor	6435.00	94	81
Aldrin	12787.50	98	89
Atrazine	7213.75	97	94
Bendiocarb	3500.00	90	95
Captan	12622.50	65	81
Carbaryl	3168.00	99	132
$\alpha$ -Chlordane	9405.00	98	94
$\gamma$ -Chlordane	9405.00	94	89
Chlorothalonil	5833.35	1	101
Chlorpyrifos	11725.35	92	89
Dacthal	5911.75	92	88
p,p'-DDE	8034.65	92	86
p,p'-DDT	25166.65	92	84
Diazinon	8833.35	100	125
Dichlorvos	3166.65	70	75
Dicofol	16333.35	121	72
Dieldrin	9666.65	92	94
Folpet	25253.75	89	88
Heptachlor	9435.00	98	94
Hexachlorobenzene	5833.35	102	107
Lindane	14035.85	96	90
Malathion	8060.50	101	83
Methoxychlor	3833.35	96	90
<i>cis</i> -Permethrin	19247.20	89	86
<i>trans</i> -Permethrin	17550.00	88	87
o-Phenylphenol	3166.65	101	98
Propoxur	1567.50	112	103
Resmethrin	76666.65	109	79
Benz(a)anthracene	2333.35	94	100
Benzo(ghi)perylene	7000.00	90	119
Benzo(a)pyrene	4666.65	71	120
Dibenzo(a,e)pyrene	4707.25	89	79
Benzo(b)fluoranthene	3166.65	81	95
Benzo(k)fluoranthene	3166.65	95	91
Chrysene	2333.35	91	91
Coronene	4733.35	88	84
Indeno(1,2,3-c,d)pyrene	3200.00	93	98
Dibenz(a,h)anthracene	3208.35	88	98
p-Terphenyl-D14	3833.35	90	87

GC/MS analysis was performed using Fisons MD800 single quadrupole instrument equipped with Lab-base software. The GC column was DB-5 (J & W Scientific) 30 m long and 0.32 mm i.d. Helium was used as the carrier gas. Injector temperature was 220°C. Analysis was performed by maintaining the oven temperature at 60°C for 5 minutes, then ramped at a rate of 15°C/min to 200°C, kept for 3 minutes at that temperature and again ramped at a rate of 15°C/min to 295°C and kept at that temperature for 15 minutes before it went back to the initial temperature of 60°C. Quantitation was performed by operating the mass spectrometer in selected ion monitoring (SIM) mode to obtain good sensitivity. Two of the most intense ions were recorded for each target analyte and the ion with highest abundance was used as the quantitation mass. The instrument was used in full scan mode only when confirmation was necessary for any analysis. Ionization was performed by 70eV electron impact.

Dual column GC/ECD was performed using Fisons GC 8000 Series instrument. The front column was DB608 (30 m × 0.53 mm i.d.) and the back column was DB1701 (30 m × 0.53 mm i.d.). Helium was used as the carrier gas and nitrogen was used as the bath gas. The oven temperature program was the same as shown for GC/MS above.

## RESULTS AND DISCUSSION

Housedust is one of the most troublesome matrices for analysis of any target analyte. Multiple cleanup is usually necessary for such a difficult matrix. Our objective was to find a cost effective way to analyze pollutants from this matrix. Therefore, single step cleanup methods were explored in this study. Percent recoveries of 28 different pesticides, 10 different PAHs and cotinine after spiking a housedust are shown in Table I. A maximum of 5% variations in results for some of the target analytes were observed in duplicate analysis. *p*-Terphenyl-D14 was used as a surrogate to monitor the extraction loss. The second column in Table I shows the GC/MS quantitation limit in terms of ppb of analyte in housedust. The high quantitation limits of permethrins were due to the presence of the compounds in high levels in the mixture. Actual quantitation limits for permethrins were 80 ppb in the instrument used in this study. The results shown in Table I were corrected for amounts detected in the unspiked housedust sample. A variation of ± 30% was taken to be acceptable limit for housedust samples. The third column shows the recovery of target analytes without any cleanup and the results clearly show a large matrix effect, since recoveries for a large number of target analytes were beyond the acceptable limit. High recoveries were observed for bendiocarb, carbaryl, diazinon, malathion, methoxychlor, propoxur and benzo(b)fluoranthene and low recoveries were observed for dicofol, resmethrin, benz(a)anthracene, and benzo(k)fluoranthene when the extract was analyzed without any cleanup. Cleanup through activated alumina lead to low recoveries for a large number of target analytes as well. The last two columns in Table I show recoveries of analytes after GPC and Florisil cleanup. These two cleanup methods showed good recoveries for all the compounds except dichlorvos, resmethrin and cotinine. The recovery problem for dichlorvos and resmethrin was later eliminated in the Florisil cleanup (Table II). Low recoveries were observed for cotinine in all the cleanup methods discussed above. There is a good analytical method for cotinine alone,<sup>5</sup> but our objective was to find a single extraction and cleanup method for all the target analytes to reduce the time and the cost of analysis. Considering the importance of cotinine as a marker compound to assess personal exposure to environmental tobacco smoke<sup>5</sup>, we decided to analyze it from uncleaned extract (101% recovery, Table I). From the results shown in Table I, it is clear that either GPC or Florisil cleanup was the method of choice. We decided to accept the cleanup through Florisil column because it is cheaper and utilized environmentally safe solvent system (10% acetone in *n*-hexane for Florisil cleanup and dichloromethane for GPC cleanup). Besides, solvent exchange will be necessary for GPC cleaned extract if GC/ECD analysis is desired for organochlorine pesticides. Florisil cleanup was used in the rest of the experiments. Cleanup efficiencies were later checked in the Florisil cleanup by varying the concentration of acetone in *n*-hexane and by increasing elution volume of the solvents. Best results (Table II) were obtained by using 20 mL of 10% acetone in *n*-hexane as the eluent. However, recovery of cotinine was still low with all the improvements in the cleanup method.

The results shown in Table I were obtained by extracting the dust immediately after spiking with the target analytes. Table II shows recoveries of the same target analytes and four additional PAHs [chrysene, dibenzo(a,e)pyrene, indeno(1,2,3-c,d)pyrene and dibenz(a,h)anthracene] from two different housedusts (Sample 1 and Sample 26) extracted 48 hours after spiking (to insure equilibration) and using the improved Florisil cleanup. Good recoveries were obtained despite delayed extraction. There was still a maximum of 5% variation for some of the analytes between duplicate analysis of each housedust sample shown in Table II. HD Sample 1 showed only 1% recovery for chlorothalonil which was the same in the duplicate extraction. No such problem was observed for HD Sample 26, which can only be explained as matrix effect.

Reproducibility of the GC/MS results for organochlorine pesticides were checked using dual column GC/ECD analysis and some of the results are shown in Table III. The GC/MS quantitation limits were not as low as the GC/ECD analysis but were very close and results were fairly reproducible.

Table IV shows results for duplicate extractions of four different housedust (carpet) samples. Time difference between extraction-A and extraction-B was two months. Considering that we were dealing with one of the most difficult matrices, the reproducibility of the results was acceptable. Sample 27 showed very high level of dieldrin, and Sample 43 showed very high level of DDT (Table IV). Presence of dieldrin and DDT was confirmed by full scan analysis of the sample extract followed by NBS library search. DDT has been out of market since the early 1970s and

dieldrin has been banned since around 1979. After further investigation on the history of the rugs in the two homes, it was found that Sample 43 was obtained from a 60-year old oriental carpet that had been in the home for 3.5 years and Sample 27 was obtained from an 18-year old carpet. Therefore, these results clearly reveal that dieldrin and DDT can be present at very high levels 20 years after use. Followup investigations are in progress in these two homes for DDT and dieldrin and their metabolites in the blood of the people living there. Sample 44 showed high levels of PAHs in the carpet dust (the carpet was 7 years old). Sample 49 showed high levels of carbaryl and permethrins although the dust was obtained from a 7-month old carpet; it appeared that the carpet was treated heavily with pesticides for indoor pest control.

Table III. Comparison of GC/MS and dual column GC/ECD results for organochlorine pesticides from housedust samples.

Compound	Sample 43		Sample 44		Sample 49	
	GC/MS	GC/ECD	GC/MS	GC/ECD	GC/MS	GC/ECD
$\alpha$ -Chlordane	55	53	33	ND	26	24
$\gamma$ -Chlordane	58	61	ND	ND	24	124
Chlorpyrifos	309	300	195	57	381	341
p,p'-DDE	5297	5803	250	255	ND	99
p,p'-DDT	103377	115177	385	223	31	40
Dichlorvos	13	ND	12	ND	ND	ND
Dicofol	2293	1574	490	363	ND	ND
Methoxychlor	13522	11954	14211	1958	ND	ND
cis-Permethrin	ND	ND	ND	ND	588410	303836
trans-Permethrin	658	ND	ND	ND	299158	174229

ND - Not detected

## CONCLUSION

Neutral pesticides and pesticides from housedusts can be analyzed by a single sequence of extraction using 6% diethyl ether in n-hexane, cleanup using Florisil column followed by GC/MS. Cotinine can be analyzed using the same extract without cleanup. High levels of DDT and dieldrin can be detected from old carpet dust 20 years after application of such pesticides. Presently a study is in progress for the development of a good analytical method for the determination of acid herbicides from housedust and soil samples.

## ACKNOWLEDGEMENTS

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Table IV. Concentration (ppb) of pesticides and PAHs in 2 g duplicate extractions of housedust samples.

Compound	Sample 27		Sample 43 (0.5 g)		Sample 44		Sample 49	
	A	B	A	B	A	B	A	B
Alachlor	ND	ND	ND	ND	ND	ND	ND	ND
Aldrin	ND	ND	ND	ND	ND	ND	ND	ND
Atrazine	ND	ND	ND	ND	ND	ND	ND	ND
Bendiocarb	ND	ND	ND	ND	ND	ND	262	13
Captan	ND	ND	ND	ND	ND	ND	ND	1282
Carbaryl	ND	ND	ND	ND	ND	ND	1163943	9978281
α-Chlordane	ND	ND	55	78	ND	ND	26	ND
γ-Chlordane	ND	ND	58	86	33	ND	24	ND
Chlorothalonil	ND	ND	ND	ND	ND	ND	ND	ND
Chlorpyrifos	1530	2293	309	306	195	240	381	309
Dacthal	ND	ND	ND	ND	ND	ND	ND	ND
p,p'-DDE	ND	ND	5297	4166	250	267	ND	86
p,p'-DDT	ND	ND	103377	157783	385	1412	31	361
Diazinon	ND	ND	ND	ND	ND	ND	649	361
Dichlorvos	ND	ND	13	ND	12	ND	ND	ND
Dicofol	ND	ND	2293	1728	490	452	ND	ND
Dieldrin	138972	110188	ND	ND	ND	ND	233	157
Folpet	ND	ND	ND	ND	ND	ND	ND	ND
Heptachlor	ND	ND	ND	ND	ND	ND	ND	ND
Hexachlorobenzene	ND	ND	ND	ND	ND	ND	ND	ND
Lindane	ND	ND	ND	ND	ND	ND	ND	ND
Malathion	ND	ND	1705	1125	ND	ND	ND	ND
Methoxychlor	656	131	13522	10345	14211	922	ND	ND
cis-Permethrin	ND	ND	ND	472	ND	ND	588410	494305
trans-Permethrin	ND	ND	ND	520	ND	ND	299158	246331
o-Phenylphenol	1118	994	484	352	784	594	ND	ND
Propoxur	ND	10	40	ND	ND	14	26	ND
Resmethrin	3279	3281	ND	ND	7118	6094	1467	5723
Benz(a)anthracene	2330	1584	4472	4423	15634	14174	992	1092
Benzo(ghi)perylene	3428	2552	4576	4670	12313	19753	1174	1243
Benzo(a)pyrene	4223	1882	6321	5655	22003	24326	1329	1485
Benzo(b)fluoranthrene	6334	5655	7976	7194	29271	30373	1927	2321
Benzo(k)fluoranthene	5216	4551	5982	6475	21129	25503	1357	1360
Coronene	86	87	454	334	1349	2078	77	33
Surrogate Recovery:	106	119	107	104	110	110	97	96

ND- Not detected

B extracted 2 months after A

**A PILOT STUDY FOR MEASURING ENVIRONMENTAL EXPOSURES FROM AGRICULTURAL APPLICATIONS OF PESTICIDES: AN OVERVIEW**

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**ABSTRACT**

A four-farm pilot study was conducted during May and June 1992 in southeastern Minnesota to test and evaluate a variety of different sampling methods for determining the potential human exposure of farm applicators and their families to 26 different pesticides during routine agricultural pesticide applications.

The study design incorporated sampling methods that included the potential routes of exposure through inhalation, ingestion, and dermal adsorption. This paper includes a discussion of the study design, the sampling rationale, and a profile of the different types of environmental samples collected from air, soil, house dust, dermal patches and gloves, diet (drinking water, solid food, and beverages), and biological samples (blood and urine).

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. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

**BACKGROUND**

The US Environmental Protection Agency (USEPA), in collaboration with the National Cancer Institute (NCI), agreed to conduct a series of pilot studies to test methods for assessing the human exposure to selected pesticides commonly used in agriculture. The principal objectives of the pilot studies are to develop and improve sampling and analytical methods to be used in a large-scale, multi-media, 200 farm human exposure study of farm pesticide applicators and their families. The large-scale study is currently scheduled to start during FY-94 with the survey of 75,000 registered pesticide applicators selected from North Carolina and Iowa.<sup>1</sup>

**STUDY DESIGN**

The multi-media, multi-seasonal, sampling design developed by the USEPA for use in the Nonoccupational Pesticide Exposure Study (NOPES)<sup>2</sup> was used as the foundation for the initial approach to be used in this study. The draft questionnaires evaluated during the pilot study included pesticide usage and application practices, health, diet, activity pattern, and safety issues.

The initial pilot study was conducted in south central Minnesota over a three-week period. The farms were selected from a cohort of licensed farm pesticide applicators being studied by Dr. Vincent F. Garry of the University of Minnesota. Dr. Garry is Director of the University's Laboratory of Environmental Medicine and Pathology, located in Minneapolis, Minnesota. His selection of the four farms was based on their reported use of the target chemicals (Table 1), their willingness to participate, and their diversity of agricultural practices, such as: the cultivation of grains, corn, and/or beans, and the raising of livestock.

#### **SAMPLING STRATEGY**

The field sampling of the farms (Table 2) was conducted during the period of 26 May through 15 June 1992. Five days was required at each location which included three days of environmental sampling. The 72-hours of ambient air sampling was divided into three consecutive 24-hour periods at each location. The five day activity and sampling schedule as defined below was proposed to be followed at each of the farms. This complex sampling approach attempted to include sampling periods identified as pre-application, application, and post-application for a variety of different pesticides.

DAY 1 Orientation: The environmental sampling and questionnaire administration team arrived at the farm and selected the residential indoor, outdoor, and pesticide storage area or barn sampling locations, administered the EPA Pesticide Usage and Activity Pattern questionnaire, set-up the portable meteorological monitoring station, discussed the proposed dermal and respiratory sampling plans, explained and demonstrated the operation of the sampling pumps, determined the carpet area for the collection of the house dust sample, determined the locations for the collection of soil samples, explained the proposed three-day sampling schedule to the family, and answered any questions raised by the participants. Air exchange rate emitters and detectors were placed throughout the house to monitor the air exchange rate over the next seventy-two hours.

The bio-medical collection team furnished the containers and the information necessary for the proper collection and storage of the DAY 2 early morning urine samples from the applicator and spouse.

DAY 2 Pre-application: The environmental sampling and questionnaire administration team returned and set-up the calibrated air samplers required for the collection of ambient indoor, outdoor (adjacent to the house), and pesticide storage or interior barn area and initiated sampling. Additionally, the team provided the applicator with a calibrated personal respiratory air sampling pump, a pair of pre-cleaned cotton gloves, and gauze patches. The patches were to be worn on the nape of the neck (on

top of the shirt) and on the front of each thigh (on top of the trousers). These sampling devices were used to estimate the applicator's pesticide exposure throughout the day's pre-application activities (approximately 12 hours). At the conclusion of the day's activities the farmer provided a hand-wipe sample prior to performing any routine personal hygiene procedures. The team made a video and still photo/slide record of the exterior physical layout of the farm including: buildings, pesticide application equipment, and residence with relationship to cultivated and/or livestock areas and a portion of the pre-application activities the applicator performed during the day. The pesticide application schedule for the following day was confirmed. The NCI/EPA Pesticide Usage and Health questionnaire was administered.

The bio-medical collection team arrived and collected the pre-pesticide application urine and blood samples from the farmer and spouse. The urine samples were to be the first specimen of the day. The team left additional urine specimen containers for the applicator's initial post application urine specimen (before retiring on DAY 3) and for the additional specimens scheduled to be collected on DAY 4 from the farmer, spouse, and up to two children.

The dietary collection team provided the containers and necessary instructions for the proper collection and storage of the dietary samples (water and food) scheduled for collection on DAY 3.

The applicator's personal respiratory sample, glove, gauze patches, and hand-wipe samples were collected at the end of the day's activities.

DAY 3 Application: The environmental sampling and questionnaire administration team returned and provided the applicator a replacement personal respiratory air sample, a new set of pre-cleaned cotton gloves, and gauze patches. These samples were provided prior to the initiation of any pesticide preparation or application activities. The team made a video and still photo/slide record of each step and the estimated time required in the handling, mixing, loading, and initial application of the pesticide formulation. A sample of the formulation was collected for laboratory analysis at this time and at any time the formulation was changed until the pesticide application activities were completed. The DAY 2 indoor, outdoor, and pesticide storage or interior barn area air samples were collected and replaced with DAY 3 samples. If the pesticide application activity was interrupted for the dinner meal, the personal respiratory air, gauze patch, glove, and hand-wipe samples were collected and replaced with new samples for the remainder of the afternoon pesticide application activities. In addition to the hand-wipe sample collected from the applicator, up to two hand-wipe samples were collected from the children who had volunteered to participate in the remainder of the study. At the conclusion of the pesticide application activities

for the day, a final hand-wipe sample was collected from the applicator following the removal of the last glove sample, and from the same children who had volunteered earlier to provide these samples and a urine specimen on DAY 4. These hand-wipe samples were collected prior to any hand washing or other normal cleanup procedures and immediately following all pesticide application activities.

The dietary collection team administered its questionnaire and also collected second plate dietary samples of the food and beverages served during the three meals on this day. Additionally, they collected a water sample from the main source of drinking water for the family.

The applicators agreed to provide a post-application urine specimen prior to retiring for the evening in a container provided by the bio-medical team and refrigerated until picked-up the next day.

DAY 4 Post-application: The environmental sampling and questionnaire administration team returned and collected the DAY 3 samples and replaced them with DAY 4: indoor, outdoor, pesticide storage or barn, personal respiratory air samples, glove, and gauze patch samples. If the previous day's pesticide activity continued then an identical procedure was followed from DAY 3 for the collection of dermal (glove and gauze patches), personal air, and hand-wipe samples from both the applicator and up to two children. The house dust sample was collected utilizing the High Volume Small Surface Sampler (HVS3), Cascade Stack Sampling Systems, Inc. of Bend, Oregon and the principal entryway and two pathway soil samples were collected as manual surface scrapings. At the conclusion of the day's activities the team collected the respiratory air sample, glove, gauze patch, and hand-wipe samples from the applicator and the air exchange rate emitters and detectors from the house.

The bio-medical collection team returned and collected the post-pesticide application early morning urine and blood sample from the applicator and spouse, and the refrigerated urine specimens from up to two different children following the guidelines used in DAY 2. If the pesticide activity was continued from the previous day, then an additional post-application final urine sample was provided by the applicator prior to retiring for the evening. Regardless of whether or not the DAY 4 activities included any pesticide application activity, a final post-application urine sample container was provided to the applicator for a final urine specimen to be collected on the morning of DAY 5.

The dietary collection team returned and collected the previous day's diet samples and completed any missing information required for the dietary questionnaire.

DAY 5 Wrap-up: The environmental sampling and questionnaire administration team returned and collected the DAY 4 indoor, outdoor, personal respiratory air, and pesticide storage or barn air samples, associated sampling equipment, and the portable meteorological monitoring station. The team completed any missing information required by the EPA and/or NCI EPA questionnaires.

The bio-medical collection team returned and collected any biological samples obtained during DAY 4 and the final post-application urine specimen provided by the applicator on the morning of Day 5.

The environmental sampling and questionnaire administration team reviewed a written record of any questions raised during the study by the participants and any responses provided to the participants. The team then proceeded to the next farm location.

#### **SUMMARY**

An analysis of the methods development and sampling design pilot study results indicated several adjustments to the study and sampling design were needed to be evaluated during the next pilot effort. The results indicated that additional methods development research was required for several of the media, particularly for soil, house dust, blood and urine. The test questionnaires did not adequately address the activity patterns of the spouse, children, or the applicator during non-application periods when linked to the exposure data for the same periods. Lastly, a more comprehensive biological and hand wipe sampling approach will be incorporated in the revised design for the spouse and children. Despite several minor problems encountered during the initial pilot effort, the overall study and sampling design proved to be workable and capable of producing a complex profile of multiple routes of exposures to pesticides used in agriculture. A more detailed discussion of the study results are presented in several additional papers and posters during this symposium.

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**TABLE 1. AGRICULTURAL HEALTH STUDY (AHS)**

LIST OF TARGET CHEMICALS			
<b>HERBICIDE</b>	atrazine metolachlor	2,4,-D salts trifluralin	alachlor dicamba
<b>INSECTICIDE</b>	carbaryl malathion propoxur dieldrin DDE	chlorpyrifos permethrin heptachlor DDT alpha-chlordane	phorate diazinon aldrin DDD gamma-chlordane
<b>FUNGICIDE</b>	dacthal folpet	captan pentachlorophenol	dicloran

TABLE 2.

**AGRICULTURAL HEALTH STUDY (AHS)  
FIELD SAMPLING DESIGN**

NUMBER OF SAMPLES COLLECTED PER FARM						
Matrix	Day 1	Day 2	Day 3*	Day 4	Day 5	Sub-Total
Indoor Air		1	1	1		3
Outdoor Air		1	1	1		3
Personal Air		A	A <sup>1</sup>	A <sup>1</sup>		3 - 5
Hand Wipe		A	A <sup>1</sup>	A <sup>1,3</sup>		2 - 5
			C <sub>a</sub> <sup>1</sup> C <sub>b</sub> <sup>1</sup>	C <sub>a</sub> <sup>1,3</sup> C <sub>b</sub> <sup>1,3</sup>		2 - 8
Gloves		A	A <sup>1</sup>	A <sup>1,3</sup>		2 - 5
Gauze Patches		A	A <sup>1</sup>	A <sup>1,3</sup>		2 - 5
House dust				1		1
Soil				3		3
Food			3 <sup>2</sup>			3
Water			1			1
Blood		A		A		2
		S		S		2
Urine		A <sup>(AM)</sup>	A <sup>(PM)</sup>	A <sup>(AM)</sup> A <sup>3(PM)</sup>	A <sup>(AM)</sup>	4 - 5
		S <sup>(AM)</sup>		S <sup>(AM)</sup>		2
				C <sub>a</sub> <sup>(AM)</sup> C <sub>b</sub> <sup>(AM)</sup>		2
Storage Building		1	1	1		3
Formulation			1	1 <sup>3</sup>		1 - 2
<b>GRAND TOTAL</b>		11	15-21	14-27	1	41-60

A = Applicator

S = Spouse

C<sub>a</sub> = Child aC<sub>b</sub> = Child b

1

If the applicator comes in for the noon meal and continues the application in the afternoon, there will be an afternoon sample collected.

2

There will be a food sample collected for each of the three meals for farm number 2 and 3.

3

If the pesticide activity has continued from the previous day.

\*

Proposed day of pesticide application.

# **ANALYTICAL METHODS FOR ASSESSING THE EXPOSURE OF FARMERS AND THEIR FAMILIES TO PESTICIDES**

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## **ABSTRACT**

In the summer of 1992, the pre-pilot phase of the NCI/EPA Agricultural Health Study (AHS) was initiated to evaluate environmental sampling and analysis methods for assessing the exposure of farm workers and their families to selected pesticides used in and around the farm. Sampling media consisted of polyurethane foam (PUF) for ambient and breathing zone air monitoring; gloves,  $\alpha$ -cellulose patches and isopropanol handwipes for personal exposure monitoring; and soil and housedust samples for environmental monitoring. An initial target compound list of 26 herbicides, insecticides and fungicides was selected. The target compound list was supplemented, for selected samples, with two insecticides and two herbicides following field sampling. The pesticides were separated into three classes: organochlorine pesticides, organophosphates and carbamates, and acids. The wide variety of matrices and pesticides presented a challenge since no single extraction method or analytical method could be used for all matrices or for all target analytes. This presentation will describe the extraction and analysis methodology used for this project. In addition, method validation results, laboratory spike results and blind external audit sample results are presented.

## **INTRODUCTION**

The Environmental Protection Agency (EPA) and the National Cancer Institute (NCI) have planned a long-term epidemiologic study of farm workers and their families to identify and quantify cancer risks among farmers and to develop an exposure assessment strategy concerning agricultural exposures to pesticides. In 1992, EPA and NCI initiated a pre-pilot study to assess exposure assessment and analytical methods for the proposed farm worker study.

Specific objectives for the analytical portion of study included: 1) Produce analytical data of good quality in order for EPA and NCI to accurately evaluate the sampling scheme. 2) Obtain sufficient data to make specific recommendations as to the appropriateness of the proposed approach. 3) Obtain sufficient data to make specific recommendations as to where further developmental work is required. 4) Obtain sufficient data to make recommendations as to how the analysis scheme could be revised to obtain data in a more cost efficient manner without compromising the quality of the data.

This paper describes the analytical approach, method validation results and blind spike audit sample results used for the 1992 study.

## **ANALYTICAL APPROACH**

A list of the target pesticides chosen for the 1992 Agricultural Health Study (AHS) pre-pilot study is given in Table I. In this table, the analytes are arranged in analytical groups. Organochlorine pesticides were determined by dual column gas chromatography using 30 m  $\times$  0.530 mm i.d. DB5 and DB608 columns with electron capture

detection (GC/ECD) on a HP 5890A gas chromatograph. Other nonchlorinated neutral pesticides, i.e., carbamates and organophosphate pesticides, were determined by gas chromatography-mass spectrometry using selected-ion monitoring (GC/MS-SIM) on a Fisons MD-800 GC/MS using a 30 m x 0.320 mm i.d. DB5 column. Confirmation analysis of neutral pesticides was performed using GC/MS operating in a full scan mode. The acids and phenols were determined by dual column GC/ECD following diazomethane derivatization. Other pesticides were added to the target list when opportunities arose to monitor their application and when they could be included into the existing analytical scheme. Additional analytes included 2,4-D isooctyl ester and lindane, which were grouped with the other organochlorine pesticides; pyrethrins, which were grouped with the other neutral nonchlorinated pesticides; and Pursuit® which was derivatized then analyzed by GC/MS-SIM.

Table I. List of target compounds by analytical groups.

Target compounds	
<b>Organochlorine Pesticides</b>	
Atrazine	4,4'-DDT
Alachlor	Dieldrin
Metolachlor	Heptachlor
Trifluralin	Permethrin
Aldrin	Captan
α-Chlordane	Dachtal
γ-Chlordane	Dichloran
4,4'-DDD	Folpet
4,4'-DDE	
<b>Organophosphates and Carbamates</b>	
Carbaryl	Malathion
Chlorpyrifos	Phorate
Diazinon	Propoxur
<b>Acids and PCP</b>	
2,4-D Salts	
Dicamba	
Pentachlorophenol	

Sampling media consisted of α-cellulose patches, cotton gloves, polyurethane foam (PUF) plugs, quartz microfiber filters, handwipes, housedust and surface soil. Detailed descriptions of the sampling media and sampling methods have been described elsewhere in this proceeding.<sup>1</sup> Sampling media, except handwipes, were extracted for neutral pesticides using Soxhlet extraction with 6% diethyl ether in n-hexane.<sup>2</sup> When required, the neutral extracts were split into two fractions for organochlorine and organophosphate/carbamate determinations. Cellulose patches, gloves, PUF, and quartz filters were extracted for acids and phenols using 1:1 diethyl ether in n-hexane acidified to pH 2 with HCl. Soil and housedust were extracted with a modified version of EPA Method 8150.

Isopropanol handwipe samples, consisting of SOF-WICK cotton gauze wetted with 50 mL of isopropanol, were extracted with two 50 mL portions of 1:1 ether in hexane. The extract was then concentrated and, when required, split into fractions for organochlorine pesticide and organophosphate/carbamate determinations. An additional fraction was then derivatized with diazomethane for determination of acids and phenols.

Since the determination of acid and neutral pesticides required separate extractions for all media except the handwipes; and the gloves, cellulose patches, PUF plugs and quartz filters could not reliably be separated into portions for neutral and acid extraction, the analytical scheme was simplified by separating the media into two sampling groups, i.e., those samples that were associated with a mixer/loader/appliator event (MLA samples) and those that were not associated with an application event (environmental samples). Specifics of the sampling scheme are described elsewhere in this proceeding.<sup>3</sup> Those samples that were associated with an MLA event and could not be separated were analyzed only for the analytical group that contained the applied pesticide. When a mixture of pesticides was applied that contained target analytes in more than one analytical group, the EPA technical project officer selected the analytical group to be targeted for analysis. Environmental samples that could not be separated were extracted and analyzed for neutral (organochlorine and organophosphate/carbamate) pesticides. Samples that could be reliably separated (e.g., housedust and soil) or media that were efficiently extracted for all analytical groups (e.g., handwipes) were analyzed for all target analytes.

## METHOD VALIDATION

A series of experiments were performed to validate the extraction of selected neutral pesticides and acid herbicides from PUF,  $\alpha$ -cellulose patches and gloves. Three replicates of each medium were spiked with 1.125  $\mu$ g each of atrazine, alachlor, metolachlor, trifluralin, dicloran, phorate, dicamba, 2,4-D, and pentachlorophenol (PCP). The acid herbicides 2,4-D, and dicamba were spiked in their free acid form. Each of the spiked media were then Soxhlet extracted using 6% diethyl ether in hexane. Results for three replicates of PUF, gloves and body patches are given in Table II. Results are comparable for all three media. Good recoveries were obtained for most of the neutral pesticides. Trifluralin results were consistently low for all three media, with essentially no recovery reported from the  $\alpha$ -cellulose patch. Low recoveries were observed for phorate from PUF and cellulose but not the gloves.

Acid herbicide recoveries for the three media were poor. PCP, which is least acidic of the three acids, was recovered most efficiently. These results are not totally unexpected since the extraction procedure was not tailored to acid extraction and indicate that in order to obtain good recoveries for neutral pesticides and acid herbicides from these personal monitoring media, separate extraction methods are necessary.

In order to validate the extraction method for acid herbicides from personal monitoring media, two quartz microfiber filters were spiked with 75 ng each of dicamba (as the free acid), 2,4-D dimethyl amine salt and PCP. The filters were extracted with acidified 1:1 ether:hexane as described above, derivatized and analyzed by GC/ECD. Recoveries of the acid herbicides were calculated and are reported in Table III. Average recoveries were greater than 50% for all three target analytes.

Method validation studies were conducted on soil and housedust to determine extraction efficiencies for selected neutral pesticides (using Soxhlet extraction) and acid herbicides (using the modified EPA method 8150) as described in the Analytical Approach section above. To test extraction of the neutral pesticides, two 2 g portions of a housedust sample obtained from a home in San Antonio were spiked with selected neutral pesticides. The spiked portions and two additional housedust portions were then Soxhlet extracted. To test the extraction of acids, two 20 g portions of soil, obtained from the SwRI grounds, were then spiked and extracted with two 20 g soil blanks by Soxhlet extraction. Two 2 g portions of the housedust sample were then spiked with 2,4-D, dicamba and PCP. The spiked portions and two additional housedust portions were then extracted using the modified EPA Method 8150. Two 20 g portions of soil were then spiked and extracted with two 20 g soil blanks, also by EPA Method 8150. A list of target analytes, spike levels, soil and housedust blank results and recovery results are given in Tables IV and V. All neutral pesticides were recovered with good efficiency from soil with the exception of trifluralin. The acid herbicides dicamba and 2,4-D were extracted with approximately 50% efficiency. However, PCP recovery was very low on both replicates (3% and 4%).

Recoveries of neutral pesticides from housedust were good with the exception of trifluralin and propoxur in Replicate I (25% and 33% respectively) and atrazine in Replicate II (41%). Recoveries for PCP were higher from housedust than from soil (29% and 24%).

Table II. PUF, glove, and cellulose patch recovery results (%) (neutral extraction).

Target Analyte	I	II	III	Mean
<b>PUF</b>				
Atrazine	118	116	123	119
Alachlor	116	122	116	118
Metolachlor	83	88	86	86
Trifluralin	59	60	58	59
Dicloran	94	93	90	92
Phorate	69	69	58	65
Dicamba	ND	ND	ND	-0-
2,4-D	2	2	ND	1
Pentachlorophenol	36	19	41	32
<b>Gloves</b>				
Atrazine	129	133	136	133
Alachlor	95	80	127	101
Metolachlor	65	53	88	69
Trifluralin	52	46	69	56
Dicloran	87	68	109	88
Phorate	99	96	104	100
Dicamba	ND	ND	1	1
2,4-D	14	ND	2	5
Pentachlorophenol	57	45	76	59
<b>Cellulose Patches</b>				
Atrazine	79	95	83	86
Alachlor	112	110	117	113
Metolachlor	84	81	86	84
Trifluralin	ND	4	1	2
Dicloran	15	34	27	25
Phorate	51	63	68	61
Dicamba	3	3	1	2
2,4-D	4	2	1	2
Pentachlorophenol	57	63	65	62

Table III. Recoveries for acid herbicides from quartz microfiber filters. Theoretical final concentration for all extracts was 0.075 ng/ $\mu$ L.

Target Analyte	I		II	
	DB5	DB608	DB5	DB608
Dicamba	60%	52%	74%	66%
2,4-D Salt	42%	45%	57%	64%
Pentachlorophenol	124%	57%	95%	70%

Table IV. Recoveries of selected neutral pesticides and acid herbicides from soil.

Target Analyte	Soil Blank Results (ng/g)			Spike Level (ng/g)	Soil Spike Results (ng/g)		% Recovery	
	I	II	I		II	I	II	
	Alachlor	0.650	1.30		10	10.16	10.70	95
Atrazine	<1.00	<1.00	15	18.00	18.50	120	123	
$\gamma$ -Chlordane	0.061	<0.250	5	5.34	5.08	107	102	
Trifluralin	<0.250	0.050	5	2.23	2.70	45	54	
Chlorpyrifos	<0.500	<0.500	10	13.07	13.34	131	133	
Diazinon	<0.500	<0.500	10	13.89	15.55	119	155	
Propoxur	<1.000	0.800	10	15.70	15.90	157	151	
Dicamba	<8.34	1.667	166.67	83.83	81.22	50	48	
2,4-D	<8.34	5.00	166.67	107.96	103.26	64	59	
Pentachlorophenol	<8.34	<8.34	166.67	5.00	6.67	3	4	

Table V. Recoveries of selected pesticides and acid herbicides from housedust.

Target Analyte	Blank Results ( $\mu$ g/g)			Spike Level ( $\mu$ g/g)	HD Spike Results ( $\mu$ g/g)		% Recovery	
	I	II	I		II	I	II	
	Alachlor	0.050	<0.125		5.0	3.700	3.988	73
Atrazine	0.025	<0.500	7.5	7.989	3.050	107	41	
$\gamma$ -Chlordane	0.286	0.182	2.5	2.891	3.086	104	116	
Trifluralin	<0.125	<0.125	2.5	0.633	1.512	25	60	
Chlorpyrifos	1.054	1.088	5.0	7.712	8.436	133	147	
Diazinon	1.675	0.939	5.0	7.737	8.556	121	152	
Propoxur	0.350	0.400	5.0	1.725	4.050	33	73	
Dicamba	<0.125	0.050	2.5	1.18	1.03	47	41	
2,4-D	<0.125	<0.125	2.5	1.73	1.47	69	57	
Pentachlorophenol	0.050	<0.1256	2.5	0.77	0.59	29	24	

An experiment was then performed to determine the recovery of selected neutral pesticides and acid herbicides from isopropanol handwipes. Three SOF-WICK pads were each moistened with 100 mL of isopropanol. A volume of a spike solution of acid herbicides and neutral pesticides was spiked into the moistened wipe at a level of each analyte of 1.125  $\mu$ g. The handwipes were then extracted as described in the Analytical Approach section above. One portion of the extracts was then derivatized for analysis of acid herbicides. Recoveries for the target analytes were calculated and are given in Table VI. Unlike the Soxhlet extraction method, good recoveries were obtained for both neutral pesticides and acid herbicides in a single extraction. As also observed for personal exposure media, the average recovery for phorate was low (7%).

Table VI. Handwipe recovery results (%).

Target Analyte	I	II	III	Mean
Atrazine	96	107	89	97
Alachlor	116	116	107	113
Metolachlor	105	98	79	94
Trifluralin	63	64	56	61
Dicloran	85	79	70	78
Phorate	6	10	6	7
Dicamba	65	65	78	69
2,4-D	83	82	98	88
Pentachlorophenol	65	63	77	68

### AUDIT SAMPLE RESULTS

Blind spike audit samples were provided by AREAL. Four PUF plugs, three quartz filters, three portions of housedust from field samples and three portions of surface soil from field samples were spiked, then shipped to SWRI for analysis using the approach described above.

Each of the four PUF plugs was extracted and analyzed for neutral pesticides. Results and biases are given in Table VII. For samples PE-PF-1 and PE-PF-2, biases were less than +/- 20% except for a large negative bias for lindane (-33%) for PE-PF-1. All pesticides reported for PE-PF-3 had a large negative bias suggesting that a dilution error or other systematic error occurred.

Table VII. PUF audit sample results

Analyte	PF-PE-1 (ng)			PF-PE-2 (ng)			PF-PE-3 (ng)			PF-PE-4 (ng)
	Spiked	Reported	Bias %	Spiked	Reported	Bias %	Spiked	Reported	Bias %	Reported
Atrazine	100	106	6.0	498	520	4.4	996	770	-23	<QL
Alachlor	103	90	-13	515	550	6.8	1030	780	-24	<QL
Chlorpyrifos	100	98	-2.0	499	480	-3.8	998	776	-22	<QL
Diazinon	99	101	-9.0	495	495	-2.2	992	741	-26	11
Propoxur	102	116	14	510	576	13	1020	753	-26	<QL
Lindane	108	72	-33	540	640	19	1080	870	-19	<25
PCP	100	NA		500	NA	-	1000	NA		NA

The three quartz filter samples were all spiked with the acid herbicide dicamba. However, only two of the three filters, Samples QF-PE-2 and QF-PE-3, were extracted and analyzed for acids and phenols. These two samples showed good results with biases of -11% and 14% respectively. These results are given in Table VIII.

Table VIII. Quartz filter audit sample results.

Analyte	QF-PE-1			QF-PE-2			QF-PE-3		
	Spiked	Reported	Bias %	Spiked	Reported	Bias %	Spiked	Reported	Bias %
Dicamba	0.95	NA	-	47	42	-11	95	108	14

Results of performance evaluation soil and housedust samples are given in Table IX. Recoveries were consistently low for the neutral pesticide extraction in both media. Since only one replicate of each medium was analyzed for neutral pesticides, it cannot be determined whether the compounds were extracted with low efficiency or an error was made in the final dilution. Large biases were observed for acid herbicides results indicating that an improved extraction and/or cleanup method is required.

Table IX. Soil and housedust audit sample results ( $\mu\text{g/g}$ ).

Analyte	Blank	IA-SE-4-PEA			IA-SE-4-PEN		
		Spiked	Reported	Bias %	Spiked	Reported	Bias %
<b>Soil</b>							
Atrazine	0.106	0.100	NA	-	10.00	7.80	-23
Alachlor	0.260	0.103	NA	-	10.00	7.75	-25
Chlorpyrifos	0.135	0.100	NA	-	10.00	7.60	-25
Diazinon	0.316	0.099	NA	-	9.92	6.35	-39
Propoxur	<0.002	0.102	NA	-	10.20	9.05	-11
Lindane	0.005	0.108	NA	-	10.80	8.00	-26
Dicamba	0.038	0.095	0.042	-96	9.46	NA	
Pentachlorophenol	0.012	0.100	0.024	-88	10.00	NA	
Analyte	Blank	3-HD-4-PEA			3-HD-4-PEN		
		Spiked	Reported	Bias %	Spiked	Reported	Bias %
<b>Housedust</b>							
Atrazine	<0.013	0.100	NA	-	10.0	4.53	-55
Alachlor	1.081	0.103	NA	-	10.0	4.32	-68
Chlorpyrifos	<0.026	0.100	NA	-	10.0	5.68	-43
Diazinon	0.051	0.099	NA	-	9.9	5.05	-49
Propoxur	<0.052	0.102	NA	-	10.0	4.95	-50
Lindane	0.006	0.108	NA	-	11.0	4.48	-59
Dicamba	0.104	0.095	0.099	100	9.5	NA	-
Pentachlorophenol	0.219	0.100	0.339	640	10.0	NA	-

## CONCLUSIONS

Neutral target pesticides were generally recovered well from spiked PUF plugs, quartz filters, soil, cellulose patches and handwipes. Recovery of neutral pesticides from housedust was inconsistent and lacked reproducibility. Good recoveries were obtained for acid herbicides from quartz filters and handwipes but acid recoveries were low from soil and housedust. The extraction of acid herbicides from gloves and cellulose patches still must be investigated. Handwipes appear to be a simple sampling method that provides good analytical results for a wide range of both neutral and acidic compounds. However, the wipe removal efficiency of these compounds from hands and other surfaces is unknown and is a vital need to assess the utility of the handwipe method as a tool for pesticide exposure assessment. Studies have recently been undertaken to improve analytical methods for the determination of pesticides in housedust. Preliminary results for these studies have been presented in this proceeding.<sup>4</sup>

Finally, the utility of separate analytical techniques for organochlorine and other neutral pesticides is questionable. State-of-the-art GC/MS-SIM instrumentation is capable of detection limits close to those obtained by dual column GC/ECD. This means that all targeted neutral pesticides can be determined with a single technique with no significant loss of detection limit.

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**NCI/EPA AGRICULTURAL HEALTH STUDY (AHS):  
DEVELOPMENT OF THE BIOMARKER QUESTIONNAIRE**

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**ABSTRACT:**

The National Cancer Institute (NCI), the Environmental Protection Agency (EPA), and the National Institute of Environmental Health Sciences (NIEHS) have planned a long-term prospective epidemiologic study of men, women, and dependent children in agricultural areas to identify and quantify cancer risks that may be associated with pesticide usage. This paper covers the types of questionnaires that are to be used in the study. The main topic is the EPA developed questionnaire that was designed to assess total pesticide exposure to the farm family.

The EPA developed a questionnaire to assess previous pesticide use and practices, exposure while pesticides are being applied, and any residual that may find its way into the home. The questionnaire was administered to 3 farm families during the spring of 1992. Activity logs were kept by participants during the one week study period. A food frequency log was kept of all food prepared during the day of application and information was gathered on the types of food used by the families, both locally produced and purchased from retail stores. Problems encountered during the administration of the questionnaire and steps taken to remedy the problems will be discussed.

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. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

## I. BACKGROUND

The "Agricultural Health Study: A prospective Study of Cancer and Other Diseases Among Men and Women in Agriculture" (1) is a collaborative effort between the National Cancer Institute (NCI), the U.S. Environmental Protection Agency (EPA), and the National Institute of Environmental Health Sciences (NIEHS). The major goal of this study is to establish a prospective cohort that can be followed for 10 years or more to evaluate the role of agricultural pesticide exposures in the development of cancer, neurological disease, birth defects, and other chronic disease outcomes. The prospective cohort of approximately 68,500 men and 6500 women will be obtained over a three year period from farmers and commercial pesticide applicators as they obtain or renew their pesticide application licenses in Iowa or North Carolina.

Assessment of exposure in most previous epidemiologic research on agricultural pesticides has typically been limited to the names of chemicals used, job title, and, occasionally, duration in that job title. Improvements in the area of exposure assessment is one of the most important features of this prospective study. A small subset of the large cohort will be selected for detailed exposure assessment based on the applicators responses to the 'Enrollment Questionnaire' (Q<sub>0</sub>).

## II. QUESTIONNAIRES USED

Currently there are five different questionnaires to be used in this study. The "Enrollment Questionnaire", referred to as Q<sub>0</sub>, will be administered when the applicators apply for their restricted-use pesticide license. The Q<sub>0</sub> is designed to collect personal identifiers, brief pesticide use history, and information on crops grown and livestock raised. A history of tobacco and alcohol use, diet and employment will also be collected. Each private applicator that agrees to participate in the study will be given a take-home questionnaire, the "Farmer Applicator Questionnaire" [Q<sub>1a</sub>] and one for the applicators spouse, the "Spouse Questionnaire" [Q<sub>1b</sub>]. The latter two questionnaires will seek detailed information on pesticide exposures, work practices, diet including cooking practices, and other lifestyle factors and health outcomes. The "Biomarker Questionnaire" [Q<sub>2</sub>] will collect information on environmental factors and pesticide practices during the current year. Activity diaries for an application event, participants time during monitoring, and pesticide use in the home will also be collected. The "Case-Control Questionnaire" [Q<sub>3</sub>] is a cancer-site specific questionnaire seeking risk factors relating to specific cancer types and factors important for evaluating biologic markers. The biomarker questionnaire is the subject of this presentation.

### III. BIOMARKER QUESTIONNAIRE

The Atmospheric Research and Exposure Assessment Laboratory (AREAL) agreed to collect exposure data on a small subset of approximately 200 farm applicators and their families. Environmental measurements will be obtained for the applicator, the applicator's spouse, and up to two children living on the farm during a three day period. The applicators will be selected based on their responses to the Enrollment Questionnaire. Environmental samples will be multi-media and multi-exposure consisting of personal air, indoor & outdoor air, drinking water, house dust, food, blood, urine, handwipes, dermal patches, and home surfaces & equipment wipes. A 4-farm pre-pilot study was conducted in May-June, 1992, where a prototype of the questionnaire was used. After the pilot study the questionnaire was extensively revised.

One of the uses of the information collected on the questionnaire is to aid in the interpretation of the environmental measurements. For example, we found detectable levels of a pesticide that was not being applied. This may have occurred when the farmer was performing repairs to application equipment. The questionnaire will also aid in quantifying the amount of exposure during different activities such as mixing/loading/handling and application. Diaries will obtain information to determine average times for common farm activities. The average times may then be used in a variety of exposure models.

#### QUESTIONNAIRE DESIGN

The prototype questionnaire was assembled from various sources. The framework came from the Non-Occupational Pesticide Exposure Study (NOPES) (2) and the House Dust/Infant Pesticide Exposure Study (HIPES) (3) questionnaires. Some of the questions came from a questionnaire that was used by Dr. Vince Gary, a pathologist at the University of Minnesota in Minneapolis, in his study of farmers who applied pesticide on their farms. Dr. Jack Griffith, Health Effects Research Lab in RTP, also supplied questions relating to health issues. In addition, Gerry Akland, Bob Lewis, and Andy Bond, Atmospheric Research and Exposure Assessment Lab in RTP, reviewed the questionnaire and had suggested various additions, deletions, and edits.

There were several problems with the prototype. One problem was with the children's activity log which was designed for pre-school children and was not suitable for older children. Also questions about pesticide inventories, how to record the application event, and the lack of an orderly progression of questions that went along with what was actually going on at the study site needed to be revised.

The current version has been extensively revised and is now composed of six parts. The first part is designed to collect

background information, such as the farm's physical features, past pesticide use, work practices, and an inventory of pesticides on hand. The second part collects information on a pesticide application event. The last four parts are activity logs. Personal activity logs are designed to collect information on the activities of the farmer, his spouse, and up to two of his children during the monitoring period. A house activity log was included to collect any information relating to pesticide application in or around the house but not including the monitored application event. The six parts, called the AGRICULTURAL HEALTH STUDY "Biomarker Questionnaire" [Q<sub>2</sub>] will be discussed in their order of use during a study.

#### **Part 1. AHS BACKGROUND SURVEY**

The background survey will collect general information concerning the family, the buildings on the farm, the history of the farm, the attitude of the family towards pesticides in general, previous pesticides used, and an inventory of all pesticides in and around the house. A record of all agricultural pesticides applied during the current year will be recorded and the type of application, number of acres treated, etc. The work practices section collects information on types of protective equipment the applicator uses, what actions are taken when he/she is directly exposed, how the pesticides application equipment is repaired or cleaned. A series of questions is asked regarding the types and amounts of food grown and consumed by the family on the farm. There are lists of both acute and chronic diseases that the respondent may have or had during the current year. This questionnaire is completed the day before monitoring begins or the first day of the monitoring period.

Another section, the household pesticide inventory, is designed to collect information on all pesticides stored in the house. This includes disinfectants used to clean bathrooms, as well as any pesticides used for flies or wasps. There is also a health and medication diary designed to collect information on any vitamins or over-the-counter or prescription medication taken by the participants.

#### **Part 2. APPLICATION EVENT ACTIVITY LOG**

The application event log is filled out by an interviewer for the first pesticide application of the day while the applicator is in the process of preparing the mixture to be used. The applicator will be monitored during both the mixing/loading/handling activities and during the application period. Amount to be applied, type of pesticide and any additives, type or amount of crops or livestock to be treated, and type of clothing worn including protective clothing will be recorded. Information will also be collected after completion of the application, such as how

the pesticide containers and any unused mixture was disposed of, and information about any required repairs.

### **Part 3. HOUSE ACTIVITY LOG**

The house activity log is used to capture information about any activities that may impact on the monitoring that is being done in or around the house. Primarily the information collected is about any pesticide that may have been used in the house, on the lawn around the house, or in the garden. Information that may impact on any personal exposure is collected such as who made the application, what equipment was used, and any precautionary actions that may have been taken. One question on the method of ventilation used each day in the home is asked (i.e., windows open, air conditioner on, etc.).

### **Part 4-6. FARMER'S, SPOUSE'S, AND CHILDREN'S ACTIVITY LOG**

These forms are an aid to the farmer applicator, his spouse and up to 2 children for remembering and recording their activities during the monitoring period. Start and stop time of each change in activity is recorded along with where they were and any equipment that may have been in use. The diaries will also collect information on other possible exposures such as painting, welding, driving diesel vehicles, etc. These diaries will also aid in the interpretation and analysis of blood and urine data. Family members are asked to fill the log out on a daily basis. If the children are too young to fill in the form, a parent will be asked to complete the daily log.

The activity logs will be summarized into the major activities that farm families participate in (e.g., the amount of time watching TV, working in the garden, in areas where pesticides have been applied or are being applied, and the amount of time farm applicators spend in other potential health-risk exposures such as painting, welding, driving diesel tractors, etc.).

### **SUMMARY**

This paper discusses the development of the biomarker questionnaire that will be used the Agricultural Health Study. The questionnaire was designed to collect background information on previous years pesticide usage, collect information on at least one application event, and collect information on the activities of the farm family during the three day monitoring periods. Environmental samples will be multi-media and multi-exposure consisting of personal air, indoor & outdoor air, drinking water, house dust, food, blood, urine, handwipes, dermal patches, and home surfaces & equipment wipes.

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# MEASUREMENTS TO ASSESS EXPOSURE OF THE FARMER AND FAMILY TO AGRICULTURAL PESTICIDES

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## ABSTRACT

Rates of dermal and respiratory exposure of four farmers to four herbicides and two insecticides were measured during nine mixing/loading/application events. Total dermal exposure (if unprotected by clothing) ranged from 3 to >4800 mg/h (median 18 mg/h) during prolonged herbicide mixing/applications and from 130 to 140 mg/h during brief insecticide applications. Respiratory exposure (median 0.008 mg/h) was 0.4 to 12% of handwipe dermal exposure (median 0.8 mg/h). Incidental mg levels were seen on gloves on non-application days, usually to pesticides applied in the prior month. Occupational exposures of the farmer predominated the residential exposure of the farm family during the study period, as indicated by child handwipes and concentrations in indoor air, carpet dust, and drinking water.

## INTRODUCTION

A prospective Agricultural Health Study of American farmers and their families is planned to investigate the observed excess of certain cancers among agricultural workers.<sup>1</sup> A small pilot study was conducted at four farms during the herbicide application season to test environmental and biological sampling/analytical methods for assessing exposure to selected pesticides in common use. This paper presents measurements of agricultural and household pesticides on gloves, handwipes, dermal patches and personal air to characterize the personal exposure of the farmer during mixing, loading, and application. Measurements in indoor/outdoor air, dust, soil, child handwipes, and drinking water are presented to describe the residential exposure of the family.

## METHODS

The study was performed at four family farms in southern Minnesota. Farms were selected from participants in an on-going surveillance study<sup>2</sup> of farm pesticide applicators based on planned agricultural use of a target pesticide during the monitoring period (May 26-June 15), presence of children in the farm family, and diversity of agricultural practices. Sampling was performed near the end of the herbicide application season. Herbicides applied by groundboom tractor during the 72-h monitoring period included alachlor and atrazine on 65 acres of corn at Farms 1A and 1B; 2,4-D isooctyl ester mixed with a small amount of trifluralin on 40 acres of wheat at Farm 2; and imazethapyr on 220 acres of soybeans at Farm 3. Observed insecticide applications were lindane sprayed on 60 hogs at Farm 1A and natural pyrethrins from an aerosol can sprayed inside a hog barn at Farm 3. No agricultural pesticides were applied in the first 24 h (Day 1). Application of one or more agricultural pesticides occurred on Day 2 and often continued on Day 3.

The personal exposure of the farmer was monitored on Day 1 as well as during pesticide application events on Days 2 and 3. Monitored application events spanned consecutive activities with pesticide exposure potential, including handling, mixing, loading, application, maintenance, and clean-up. Sampling methods are described by Harding et al.<sup>3</sup> During the event, the farmer wore cotton gloves and patches above clothing on both thighs and the nape of the neck (to crudely estimate dermal exposure to the hands and rest of body without adjustment for the protective effect of clothing), and a breathing-zone air sampler (to estimate inhalation exposure). After removing the gloves at the end of the event, the farmer wiped both hands with two isopropanol-laced gauze pads.

Daily 24-h (10 a.m. to 10 a.m.) air samples were obtained on polyurethane foam (PUF) simultaneously inside the farm house and outside from a porch or in the yard. On Day 3, a dust sample was collected from carpeted floors in the house while surface soil was obtained at the main entryway (door mat or porch) and along the pathway from the vehicle parking area to the house. Drinking water was collected from the kitchen faucet. Handwipe samples were also obtained from each toilet-trained child after a pesticide application event.

Glove, patch, PUF, and fine (<150 µm) dust samples were Soxhlet-extracted with 6% diethyl ether/hexane and analyzed for neutral pesticides (4 herbicides, 16 insecticides, and 4 fungicides). Extracts were quantitated by gas chromatography using dual-column electron capture detection and mass spectrometry selected ion monitoring and confirmed by GC/MS in full-scan mode. Extraction and analytical methods are presented by Geno et al.<sup>4</sup> Reported results are not adjusted for recovery efficiency. Measurement contamination, accuracy and precision as indicated respectively by field blanks, spikes, and duplicates are presented by Harding et al.<sup>3</sup>

## RESULTS

A total of 79 field and duplicate samples (18 farmer exposure samples, 53 environmental samples, and 8 child handwipe samples) were analyzed for all principal target analytes. The other 37 field and duplicate samples, taken to measure the personal exposure of the farmer during agricultural application of a specific pesticide, were only analyzed for the analyte group which included this target applied pesticide. The most commonly detected analytes were alachlor (93% of field and duplicate samples), atrazine (91%), pentachlorophenol (86%), dicamba (84%), 2,4-D (78%), lindane (gamma-HCH) (71%), trifluralin (68%), captan (56%), chlorpyrifos (55%), phorate (38%), 4,4'-DDT (37%), dieldrin (36%), propoxur (36%), folpet (35%), and metolachlor (31%).

### Occupational Exposure of the Farmer

Farmers 1A and 1B received substantial exposure to alachlor during mixing, loading, and application of the formulated mixture (see event 3C for Farmer 1A and events 3A, 3B, and 4A for Farmer 1B in Table I). Farmer 1A received somewhat less exposure in transferring Lasso® from bulk containers during the baseline Day 1 (event 1A-2). Farmer 3 also received considerable alachlor exposure during normal activities on Day 1 when no pesticides were applied (event 3-2). A month earlier, Farmer 3 had spent 120 hours applying alachlor to his corn crop. Farmer 2 did not apply alachlor that spring and had low exposure (Table I).

The measured rates of dermal and respiratory exposure which these farmers received during mixing/loading and application of alachlor, atrazine, 2,4-D isooctyl ester, imazethapyr, lindane, and pyrethrins to crops and livestock are presented in Table II. If unprotected by clothing, the total dermal exposures of monitored farmers ranged from 3 to >4800 mg/h (median 18 mg/h) during prolonged herbicide mixing/application and from 130 to 140 mg/h during brief insecticide mixing/application. The crude rates of unprotected dermal exposure to the hands and the rest of the body were on the same order of magnitude, except for 2,4-D isooctyl ester, imazethapyr and a Lasso® (alachlor) mixing accident. The gloves represented from 7% to >99% of the total unprotected dermal exposure. The highest observed exposure occurred during mixing when Farmer 1B accidentally saturated one finger of a glove while opening a Lasso® container. Handwipes revealed residues of pesticides that were 0.1% to 85% (median 5%) of amounts found on gloves. The respiratory exposure rate was less than 0.1 mg/h, except for pyrethrins applied indoors by aerosol can (0.44 mg/h). The rate of respiratory exposure ranged from 0.4% to 12% (median 0.7%) of the handwipe exposure rate during mixing/application events.

The exposure of the farmer to a pesticide was generally higher by at least several orders of magnitude while he mixed and applied the pesticide than on baseline nonapplication days. However, in ten instances, the farmer's gloves contained mg levels of pesticides that had not been mixed or applied that day; in eight cases, the high incidental exposure was to a pesticide that the farmer had applied in the previous month.

Table I. Alachlor amounts ( $\mu\text{g}$ ) in personal exposure monitoring of farmers by event and matrix.

Farmer-event code	Activity codes <sup>a</sup>	Activity duration (h)	Glove pair	Handwipe		Three dermal patches	Personal air conc. ( $\mu\text{g}/\text{m}^3$ )
				Mid event	End of event		
<b>Farmer 1A</b>							
1A-2	T	8.53	18,500	270	250	51	2.6
1A-3C	MA	2.60	59,800		480	380	13.7
1A-4B	R	0.75	2,610		92	17	0.49
<b>Farmer 1B</b>							
1B-3A	MA	3.03	105,000		6,380	2,050	7.6
1B-3B	MA	5.38	270,000		14,800	5,400	11.1
1B-4A	MA	3.28	>2,370,000 <sup>b</sup>		9,540	1,020	20.3
<b>Farmer 2</b>							
2-2		7.78	11.5	0.03	0.06	0.005	ND
2-3	R	3.00	ND		0.44	0.056	0.03
2-4		6.40	ND		0.08	0.043	ND
<b>Farmer 3</b>							
3-2		6.90	4,470		36	19.7	0.43
3-3		7.02	NA		NA	NA	NA
3-4A		0.05	NA		NA	NA	NA
3-4B		7.20	NA		NA	NA	NA

ND = Not detected

NA = Not analyzed

a T = transfer from bulk container; M = mixing and loading; A = application; R = residue applied since trace found in analysis of formulated mixture.

b Gloves removed after one finger of glove was dipped in Lasso® (alachlor) during mixing 30 min after event began. Alachlor result is underestimate, since crystalline precipitate formed in glove extract.

### Residential Exposure of the Farm Family

Measurements indicative of residential exposure to pesticides at Farmhouse 1A are presented in Table III. Air concentrations were generally higher indoors than outside the farmhouse, although similar indoor and outdoor levels were observed at Farmhouse 1A for the applied analytes atrazine and lindane. Agricultural pesticides were usually present at higher concentrations in indoor carpet dust than in entryway or pathway soil. The prominent residues recovered in handwipes of the child were also prominent in the indoor air or dust (alachlor, atrazine, captan; chlorpyrifos, and pentachlorophenol at Farmhouse 1A).

Table II. Rates of dermal and respiratory exposure (mg/h) of farmers to applied analytes from personal exposure monitoring by event and matrix.

Farmer-event code	Activity codes <sup>a</sup>	Activity duration (h)	Dermal Exposure			Respiratory exposure <sup>d</sup> (personal air)
			Hands		Rest of body <sup>b,c</sup> (dermal patches)	
			Glove pair <sup>b</sup>	Handwipe after event		
Alachlor applied to corn from groundboom tractor by Farmers 1A and 1B						
1A-3C	MA	2.60	23.0	0.18	30.7	0.025
1B-3A	MA	3.03	34.6	2.10	146	0.014
1B-3B	MA	5.38	50.2	2.75	217	0.020
1B-4A	MA	3.28	>4740 <sup>e</sup>	2.91	67.2	0.037
Atrazine applied to corn from groundboom tractor by Farmers 1A and 1B						
1A-3C	MA	2.60	2.02	0.043	9.21	0.005
1B-3A	MA	3.03	0.78	0.66	9.77	0.003
1B-3B	MA	5.38	6.17	0.80	11.88	0.004
1B-4A	MA	3.28	32.0 <sup>e</sup>	1.15	24.6	0.008
2,4-D Isooctyl ester applied to wheat from groundboom tractor by Farmer 2						
2-3	MA	3.00	9.77	0.051	0.58	0.002
Imazethapyr applied to soybeans from groundboom tractor by Farmer 3						
3-3	MA	7.02	3.30	0.023	0.055	ND
3-4B	MA	7.20	2.86	0.002	0.048	ND
Lindane applied to hogs from hose sprayer by Farmer 1A						
1A-4B	MA	0.75	28.3	2.11	105	0.008
Pyrethrins applied in hog barn from aerosol can by Farmer 3						
3-4A	A	0.05	50.6	9.0	88	0.44

ND = Not detected

a M = mixing and loading; A = application.

b Not adjusted for protective effect of clothing.

c Scaled to total body surface excluding hands from dermal patch amount based on surface area.

d Based on a farmer breathing rate of 1.8 m<sup>3</sup>/h, assuming a moderate workload.

e Gloves removed after one finger of glove was dipped in Lasso® (alachlor) during mixing 30 min after event began.

## DISCUSSION

This pilot study employed a multiresidue analytical method and a multimedia sampling design to assess the exposure of the farmer and family to agricultural pesticides. The principal exposure of the farmer was to pesticides which he mixed and applied. The proportion of unprotected dermal exposure attributed to hand exposure (7% to >99%) exceeded the 27% to 99% range in studies reviewed by Franklin.<sup>5</sup> The protection afforded by cotton work gloves was highly variable: handwipes uncorrected for wipe removal efficiency showed that 0.1% to 85% of the residual glove amount had penetrated to the skin and was wiped from the hand afterward. Cotton gloves provided Farmer 1B trivial hand protection during mixing/loading/groundboom tractor application

of alachlor and atrazine; handwipes revealed similar residues on bare (event 4A) and gloved (events 3A and 3B) hands. The multiresidue analysis of glove samples established that the farmer occasionally receives incidental occupational exposures of 1 mg/h, usually to pesticides which he had applied in the prior month. Uncorrected handwipe dermal exposure dominated respiratory exposure during every application event, indicating that the dermal pathway may be the principal route of exposure for these Minnesota farmers, as found in prior studies.<sup>5</sup>

Table III. Indicators of residential exposure to pesticides at Farmhouse 1A.

Pesticide	Mean (n=3) air concentration (ng/m <sup>3</sup> )		Concentration (ng/g)			Handwipe of child (age 3) (ng)		Drinking water conc. <sup>a</sup> (ng/L)
	Indoors	Outdoors	Fine carpet dust	Entry-way soil	Path-way soil	Day 2	Day 3	
Alachlor	141	45	2,450	261	163	221	411	2
Atrazine	12	11	1,150	106	83	199	111	113
Captan	3.7	0.1	768			10	322	
Chlordane ( $\alpha + \gamma$ )	0.1	0.1	10	0.3				
Chlorpyrifos	9.0	0.8	90	135	104		179	2
$\Sigma$ DDT (DDT+DDD+DDE)	0.9		201	131	0.2	6	5	
Dacthal				0.3		2		
Diazinon			149	316				
Dicloran		0.3						
Dieldrin	0.1			65				
Folpet	0.3	1.0				2		
Lindane	15	15	12	5	11			
Metolachlor	7.1	1.0						
Pentachlorophenol	6.8	0.6	103	12	2.3	99	34	
Permethrin ( <i>cis + trans</i> )				37				
Phorate	0.3	0.1	8	1.3	0.3			
Propoxur			18			39	26	1
Trifluralin	0.7	0.1	10	0.1	0.3			

Blank = not detected

a Obtained from faucet at parents' neighboring Farmhouse 1B.

Air concentrations of recently applied herbicides were usually higher inside the farm house than outdoors. Some elevations of outdoor and indoor air concentrations were concurrent with an agricultural application.<sup>6</sup> Indoor elevation of lindane at Farmhouse 1B was traced to volatilization of residues transported on the work clothing or tracked in on the shoes of Farmer 1A during his visit following lindane spray application to his hogs.<sup>6</sup> Aerosol drift from upwind spraying appeared to elevate the outdoor air concentration in two instances.<sup>6</sup>

During the study period, occupational exposure of the farmer to agricultural pesticides greatly exceeded the residential exposure of his family. The personal air concentration breathed by the farmer during application events exceeded the home indoor air concentration by one to several orders of magnitude. Amounts of applied pesticides were three orders of magnitude higher in handwipes of the farmer than of his child.

The cost of the multiresidue analysis limited the number of samples, so that exposures were determined over entire events, rather than for component mixing/loading, application, and repair activities. Monitoring data are needed to assess relative exposure for these component activities. The three patch samples were extracted together to yield a single crude estimate of non-hand unprotected dermal exposure. Correction for the protective effects of clothing dictates that representative patches over typical bare skin areas (lower arms/face/neck) and over clothed areas be extracted separately. A means to adjust clothing surface exposure for pesticide penetration of clothing is also needed. The use of gloves greatly exaggerates hand exposure due to absorption of liquids<sup>7</sup>, while handwipes cannot recover pesticide which has been absorbed or irreversibly bound in layers of the skin. Experimental determination of wipe removal efficiency for a spectrum of agricultural pesticides may provide a valid basis to rely on the handwipe in place of the glove sample to estimate hand exposure.

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## Collection and Analysis of Duplicate Diet Samples: A Pilot Study on Farmer Exposures to Pesticides

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### ABSTRACT

A pilot study for the NCI/EPA Farm Occupation Exposure Study (NEFOES), recently renamed the Agricultural Health Study (AHS), was conducted to provide a preliminary assessment of a multi-media sampling approach for performing pesticide exposure measurements of farmers. Tests of the dietary component of the study included collection of 24-hour duplicate diet samples of all farmer-consumed foods and beverages at two farms. Drinking water was collected at three farms. Food frequency, meal selection, and food diary survey instruments were tested for recording food consumption and characterizing dietary patterns. Samples were analyzed for chemicals selected from a target list of 28 insecticides, fungicides, and herbicides. Pesticides were extracted from aliquots of food homogenates using FDA Method 211.13 and gel permeation chromatography. Extracts were analyzed by GC/MS in the selected ion monitoring mode and by GC/ECD. One beverage sample from each farm was extracted and analyzed for acid herbicides using EPA Method 515. A second beverage sample was extracted by continuous liquid/liquid extraction, then analyzed by GC/MS and GC/ECD without further clean-up. Water samples were extracted using EPA Methods 507, 508, and 515, then analyzed by GC/MS. No pesticides were measured above the estimated quantifiable limits in the food and beverage samples. Atrazine was measured at 0.15 ppb in the drinking water from one farm.

### INTRODUCTION

The U.S. Environmental Protection Agency (USEPA), in collaboration with the National Cancer Institute, sponsored a pilot study to test methods for assessing farmer exposure to 28 selected pesticides (listed in Table 1) commonly used in agriculture. Overall objectives for the pilot study included testing a multi-media sampling design, several questionnaires, and sample collection and analysis methodology for the inhalation, dermal, and ingestion exposure routes. The duplicate diet method tested in this study was designed to collect combined food samples representing total dietary intake of foods and/or beverages over a specified period of time. Only a few studies have been reported applying duplicate diet (or similar) methods to organic chemical contaminants<sup>1,2</sup>. Therefore, the primary objective of the dietary sampling was to make a preliminary test of the procedures and to identify additional work needed to refine the methods. All foods and beverages consumed by the farmers at two farms were collected over single 24-hour periods. The composite foods and composite beverages were homogenized, extracted, and analyzed using gas chromatography/mass spectrometry (GC/MS) and gas chromatography/electron capture detector (GC/ECD) methods. Preliminary versions of a food diary and dietary questionnaires were used to identify and quantify the foods collected during the study and to test methods that may be used to characterize dietary patterns. Drinking water samples were collected at three study farms using EPA methods and analyzed for most target pesticides.

## METHODS

### Study Design

Four farms were included in the pilot study, numbered 1A, 1B, 2, and 3. Farms 1A and 1B were on adjacent land that was jointly farmed by a father and his adult son. The dietary component of the study was meant only to provide a preliminary test of methods, so food and beverage samples were collected from the farmer only at Farms 2 and 3. Drinking water samples were collected from Farms 1B, 2, and 3 (Farm 1B was selected because of reported handling of pesticides near the well).

### Questionnaires

Two questionnaires were administered to the farmers providing the duplicate diet samples. The food frequency component of the NCI Health Habits and History Questionnaire was self-administered by the farmer in 25 to 35 minutes. This questionnaire was designed as a dietary recall history, recording the frequency of consumption of common individual foods<sup>3</sup>. A meal selection questionnaire was designed to test the ability to define meals normally eaten by the farmer and the frequency of consumption. It was applied by an interviewer in 10 to 20 minutes. The purpose in this pilot study was primarily to test burden of administering these questionnaires. Similar questionnaires may be used in future studies to assess if the collected foods are part of the normal diet.

### Food Collection and Analysis

The farmers at Farms 2 and 3 were instructed to prepare a second plate with the identical type and amount of food eaten at each meal or snack. Additional servings or leftovers were to be added or subtracted as necessary. The farmers were also instructed to record the name of each food on the food diary, and measure the portion size with common household measures (measuring cups, rulers, etc.). The farmers' spouses were included in the training session and assisted in collecting the foods and completing the food diary. Duplicate portions of all foods were collected by the farmers from midnight to midnight on the third study day. At the end of every meal or snack, all foods from the second plate were combined into one 4-L glass jar. The jar was stored in a foam liner inside a cooler with ice packs. Food samples were transported to the laboratory within one day and were homogenized within one day of receipt. The entire food sample was placed in a 4-L stainless steel blender container. Clean water was added incrementally to the sample while blending 15 seconds at a time at the low speed setting. Just enough water was added to achieve thorough homogenization; the amount depended on the original water content and the weight of the collected foods. A total of 200 mL was added to the 871 g sample from Farm 2, and 400 mL was added to the 520 g sample from Farm 3. Samples were blended for 2 minutes at low speed and two minutes at high speed. Aliquots of the homogenate (50 g) were transferred to glass jars and stored at -20°C.

Three multi-residue extraction methods, selected from the FDA Pesticide Analytical Manual<sup>4</sup>, were tested to determine method performance with composite food samples and spiked reagent water prior to extraction of the farm samples. These methods included 211.13, method 232.4 (modified to include a petroleum ether extraction), and method 212.13. None of the methods was applicable to the 2,4-D, dicamba, or pentachlorophenol, which were not measured in the food samples. Method 211.13 resulted in the highest overall recoveries for most of the target pesticides and was therefore used with a gel permeation chromatography (GPC) clean-up to extract 50 g portions of the collected food samples. Each food sample was mixed with potassium oxalate and 50 mL of methanol, extracted three times with 50 mL (1:1) diethyl ether and petroleum ether. The extracts were dried through anhydrous sodium sulfate, and were cleaned using a Phenogel Prep-100 GPC column eluted with methylene chloride. High concentrations of fat and other coextractive interferences remained in the extracts, which were cleaned again using GPC. The GPC effluent was concentrated to 2.0 mL and analyzed by GC/ECD. The sample was then further concentrated to 0.2 mL and analyzed by GC/MS in the selected ion mode. The conditions for GC/ECD and GC/MS were similar to those described in EPA Method 505<sup>5</sup>. Samples were fortified with the target pesticides to assess recoveries, and method blanks were used to assess background levels.

### Beverage Collection and Analysis

Beverage samples were collected in a second 4-L glass jar using the duplicate diet methods described above for foods. Samples were returned to the laboratory, where they were mixed and siphoned into clean glass jars and stored at -20°C. Sample aliquots (60 g) were extracted for acid herbicides according to EPA Method 515.1<sup>5</sup> after dilution to 1.0 L with ether-washed and acidified water (pH < 2). Acid herbicide extracts were derivatized with diazomethane. Sample aliquots (60 g) were extracted for neutral pesticides after dilution to 1.0 L with water (pH adjusted to 8.2-8.9). Extraction was performed with methylene chloride in a continuous

liquid-liquid extractor for 18 hours. Organochlorine and acid herbicide samples were analyzed by dual-column GC/ECD. Analysis of carbamates and organophosphorus pesticides, and confirmation analysis of organochlorine pesticides and acid herbicides, was performed by GC/MS in the selected ion mode. Samples were fortified with ten of the target analytes to assess recoveries, and method blanks were used to assess background levels.

#### Drinking Water Collection and Analysis

Private wells supplied drinking water at all farms in the pilot study. Drinking water samples were collected from the kitchen tap at Farms 1B, 2, and 3 and analyzed according to EPA Methods<sup>5</sup> 507/508 (neutral pesticides) and 515.1 (acid herbicides). The target pesticides were analyzed by GC/MS after extraction. Method blanks and method controls were used to assess the background and recovery of the target pesticides. The EPA Methods did not apply to carbaryl, chlorpyrifos, malathion, phorate, propoxur, captan, dichloran, and folpet. All except chlorpyrifos and propoxur were tested using the Method 507/508 extraction with GC/MS analysis. Duplicate water samples were analyzed at a second laboratory by GC/ECD and GC/MS to confirm the results.

## RESULTS AND DISCUSSION

### Food and Beverage Collection

Duplicate diet 24-hour samples of foods and beverages were successfully collected by the farmers at both farms. The 4-L glass jars and coolers were adequate for holding and storing the collected sample volumes. Food samples are bulky and difficult to store and ship in glass containers, large studies may require on-site sample processing and homogenization. Additional work should be performed on methods of identifying and collecting individual food items of local origin, especially those subject to pesticide contamination.

### Food Diary and Questionnaires

The farmers (with help from their spouses) were able to complete the food diaries, but providing detailed descriptions of ingredients and estimating portion sizes with household measures proved to be very time consuming. The farmers were observed to serve their original plates using measuring cups, possibly changing the amount of food that would have normally been consumed. It is recommended that the diary recording and food portion estimates be greatly simplified in future studies. Additional work has shown that the participant effort can be greatly lessened; foods can be stored separately by the participant, then the descriptions and size estimates can be performed by the research staff, if necessary. The farmers were able to complete the food frequency questionnaire with few problems. It was difficult to administer the meal selection questionnaire in a short time period, and both farmers had trouble defining several typical meals that would characterize their diets. Neither the food frequency questionnaire nor meal selection questionnaire would be adequate to assess whether the collected food is typical of the normal diet for a collection period of one day. Alternative questionnaires that require only 5 minutes to administer, and ask simple questions about dietary changes and meal consumption frequency, have been developed and tested.

### Food and Beverage Analysis

None of the target pesticides were measured in the food or beverage samples above the estimated method quantifiable limits (EMQL) (Table 1). EMQL values of 3 µg/kg or less were achieved for most of the target pesticides. Recoveries above 65% were achieved for 14 of the target pesticides from 50 g portions of the food sample homogenates fortified at 6 µg/kg (approximately two times the EMQL). Recoveries above 50% were measured for four other pesticides. Low recoveries were noted for atrazine, captan, folpet, and propoxur. Losses of the more volatile pesticides may have been due to the many sample manipulations required to remove interferences. Interferences also presented problems in identifying and quantifying heptachlor, cis-permethrin, and malathion. In most cases the interferences were high concentrations of fatty acids not removed by the clean-up. Additional method development is currently being directed towards minimizing sample handling, eliminating or reducing interferences, improving recoveries, and lowering limits of detection. Beverage samples were extracted and analyzed without the need for time-consuming clean-up steps. The quantifiable limits were very good for 60 g samples, particularly for the organochlorine pesticides analyzed by GC/ECD. Additional recovery studies need to be performed using all of the target analytes in samples with different beverage compositions. It is also recommended that if a separate drinking water analysis is performed that water not be collected as part of the duplicate diet sample.

### Drinking Water Analysis

Results for the analysis of the target pesticides in the farm drinking water are presented in Table 2. Atrazine was measured at 0.15 ppb at Farm 1B. Atrazine was reported to have been mixed and loaded into the sprayer within 6 m of the well at this farm on one or more occasion. No other pesticides were measured at levels above the EMQL. The EMQLs ranged from 0.02 to 0.05 ppb for analysis by GC/MS. Small amounts of 2,4-D and pentachlorophenol were measured in the method blanks. Recoveries from method controls (clean water fortified with target pesticides) were above 75% for all compounds except pentachlorophenol (62%), captan (34%), and folpet (3%). Recoveries above 130% were observed for carbaryl and cis-permethrin.

### CONCLUSIONS

The primary objective of the duplicate diet component of the NEFOES study was to provide a preliminary test of the sample collection and analysis methodology. Duplicate diet samples of foods and beverages were successfully collected and homogenized. Additional method development is needed for the identification and collection of food items of local origin to identify potential sources of dietary exposure. Estimating portion sizes with common household measures and providing a detailed food record was very time consuming for the participant and possibly resulted in nonrepresentative samples. More refined methods have been tested that will lower participant burden. Questionnaires may be used to evaluate whether the collected food samples are part of the normal diet for the participant, but if samples are collected for only one 24-hour period then it is likely that only general questions can be applied with subjective results. No target pesticides were observed above the EMQLs in the food or beverage samples from two farms. Atrazine was present in the drinking water at one farm. The extraction and analysis methods for both composite foods and beverages performed well, with low detection limits and acceptable recoveries for most target pesticides. Additional method development is ongoing to reduce interferences, improve analyte recoveries, and to reduce sample handling steps in the food extraction and analysis methods.

### ACKNOWLEDGEMENT

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TABLE 1. METHOD PERFORMANCE FOR PESTICIDES IN FOODS AND BEVERAGES

Pesticide	Composite Beverage Samples (60 g)			Composite Food Samples (50 g)		
	% Recovery Samples Spiked <sup>a</sup> at 1-8 µg/kg	EMQL µg/kg	Method Blank µg/kg	% Recovery Samples Spiked <sup>b,c</sup> at 6 µg/kg	EMQL µg/kg	Method Blank µg/kg
<b>INSECTICIDES</b>						
Aldrin	37 ± 3	0.08	ND	73	1.5	ND
Carbaryl	NT	1	0.07	52	3	ND
alpha-Chlordane	52 ± 2	0.08	ND	86 ± 11	1	1.7
gamma-Chlordane	NT	0.08	ND	61 ± 9	2	0.8
Chlorpyrifos	120	1	0.07	83 ± 30	1	ND
Diazinon	138 ± 2	1	0.05	109	3	ND
4,4'-DDD	NT	0.08	ND	82 ± 8	1	ND
4,4'-DDE	NT	0.08	ND	102	1	ND
4,4'-DDT	NT	0.08	0.04	80 ± 26	1	ND
Dieldrin	NT	0.08	ND	INT	1	ND
Lindane	NT	0.08	ND	79 ± 18	1	ND
Heptachlor	NT	0.08	0.01	INT	INT	27
Malathion	NT	1	ND	165	6	ND
cis-Permethrin	NT	0.08	ND	INT	NR	ND
trans-Permethrin	NT	0.08	ND	54	NR	ND
Phorate	NT	1	ND	58 ± 17	1	ND
Propoxur	159 ± 8	1	0.03	35	2	ND
<b>HERBICIDES</b>						
Alachlor	137 ± 11	1	ND	92 ± 3	2	ND
Atrazine	99 ± 24	1	ND	2	NR	ND
Dicamba	64 ± 6	0.08	ND	NT	NT	NT
2,4-D	42 ± 16	0.08	ND	NT	NT	NT
Metolachlor	NT	0.08	ND	111	2	ND
Trifluralin	NT	0.08	ND	52 ± 11	1	ND
<b>FUNGICIDES</b>						
Captan	NT	0.08	ND	0 ± 0	1	ND
Dacthal	NT	0.08	ND	83 ± 12	1	ND
Dichloran	NT	0.08	ND	57	2	ND
Folpet	NT	0.42	ND	0 ± 0	NR	ND
Pentachlorophenol	37 ± 6	0.08	ND	NT	NT	NT

**ABBREVIATIONS**

EMQL = Estimated method quantitation limit ND = Not detected NT = Not tested  
 INT = Interferent NR = Not reported, low recovery

<sup>a</sup> Mean and difference for one sample from Farm 2 and one sample from Farm 3.

<sup>b</sup> Values without differences represent one sample from Farm 3 analyzed by GC/MS.

<sup>c</sup> Values with standard deviations represent five samples; two each from Farms 2 & 3 analyzed by GC/ECD and one from Farm 3 analyzed by GC/MS.

TABLE 2. RESULTS OF GC/MS ANALYSIS OF PESTICIDES IN FARM DRINKING WATER

Pesticide	EPA Method	EMQL µg/L	Method Blank µg/L	Method Control % Recovery (3 or 4 tests)	Water Samples, µg/L*			
					Farm 1B	Farm 2	Farm 3	
<u>INSECTICIDES</u>								
Aldrin	508	0.025	ND	79 ± 9.6	ND	ND	ND	
Carbaryl	None	0.025	ND	148 ± 26	ND	ND	ND	
alpha-Chlordane	508	0.025	ND	91 ± 7.2	ND	ND	ND	
gamma-Chlordane	508	0.025	ND	89 ± 7.8	ND	ND	ND	
Chlorpyrifos	None	NT	NT	NT	NT	NT	NT	
Diazinon	507	0.025	ND	112 ± 5.6	ND	ND	ND	
4,4'-DDD	508	0.025	ND	94 ± 10	ND	ND	ND	
4,4'-DDE	508	0.025	ND	90 ± 7.1	ND	ND	ND	
4,4'-DDT	508	0.025	ND	100 ± 8.0	ND	ND	ND	
Dieldrin	508	0.025	ND	92 ± 5.1	ND	ND	ND	
Lindane	508	0.025	ND	90 ± 4.4	ND	ND	ND	
Heptachlor	508	0.025	ND	90 ± 8.5	ND	ND	ND	
Malathion	None	0.025	ND	116 ± 7.8	ND	ND	ND	
cis-Permethrin	508	0.025	ND	133 ± 21	ND	ND	ND	
trans-Permethrin	508	0.025	ND	117 ± 16	ND	ND	ND	
Phorate	None	0.025	ND	88 ± 5.2	ND	ND	ND	
Propoxur	None	NT	NT	NT	NT	NT	NT	
<u>HERBICIDES</u>								
Alachlor	507	0.025	ND	99 ± 7.5	ND	ND	ND	
Atrazine	507	0.025	ND	107 ± 3.5	0.15	ND	ND	
Dicamba	515	0.020	ND	77 ± 2.0	ND	ND	ND	
2,4-D	515	0.050	<0.05	83 ± 4.0	ND	ND	ND	
Metolachlor	507	0.025	ND	105 ± 8.6	ND	ND	ND	
Trifluralin	508	0.025	ND	75 ± 9.5	ND	ND	ND	
<u>FUNGICIDES</u>								
Captan	None	0.025	ND	34 ± 1.9	ND	ND	ND	
Dacthal	508	0.025	ND	93 ± 5.6	ND	ND	ND	
Dichloran	None	0.025	ND	97	ND	ND	ND	
Folpet	None	0.025	ND	3 ± 0.7	ND	ND	ND	
Pentachloropheno]	515	0.020	<0.02	62 ± 16	ND	ND	ND	

ABBREVIATIONS

EMQL = Estimated method quantitation limit    ND = Not detected    NT = Not tested

\*Analysis by GC/MS at one laboratory; confirmed by analysis at a second laboratory.

***Session 20***  
***Acid Aerosols and***  
***Philadelphia Results***

## EXPOSURES TO ACID AEROSOLS AND GASES IN SCHOOLS AND YOUTH CENTERS OF PHILADELPHIA

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### ABSTRACT

Aerosol species and gaseous components were measured utilizing Annular Denuder Systems (ADS) during June-August of 1992 inside 15 different microenvironments (schools and youth centers) in Philadelphia. For two or more weeks each, daily (12-h) samples were collected, starting at 8:00 am. Infiltration rates were monitored at each site using a perfluorocarbon tracer (PFT) technique. A sampler was operated on a nearby rooftop to provide matching outdoor data. Indoor levels of aerosol sulfate and acidity were lower than outdoor concentrations, while indoor  $\text{NH}_3$  and HONO exceeded their levels outdoors. Indoor acid aerosols were found to be correlated with the outdoor concentrations, but were substantially neutralized by indoor ammonia. Air exchange rates were generally in the range  $1\text{-}6\text{ h}^{-1}$ . The data will be used to assess whether the magnitude of children's exposures to acid aerosols pose a potential health risk and to investigate neutralization processes caused by indoor ammonia.

### INTRODUCTION

Summer is the time of year when photochemical smog occurs at its highest levels. Along with ozone, acid aerosols add to the atmospheric burden of lung irritants. While most people would like to spend their summer days outdoors, the reality is that most people are indoors much of the day. This is especially true for young people, who are often being cared for at institutional facilities, such as schools, daycares or recreational centers.

For most ambient contaminants, indoor spaces are protective, because they can reduce the exposures by limiting penetration and/or stability. As a secondary pollutant, sulfate aerosols occur in the accumulation mode, for which deposition is least effective. What has been found is that sulfate aerosols penetrate indoors with great efficiency. Furthermore, depositional losses are very low, so the infiltration efficiency for sulfate aerosols is high: frequently, indoor concentrations average close to 100% of the outdoor levels. Sulfate aerosol concentration averaged 0.96 of outdoor levels in Boston homes (Brauer et al., 1991). Penetration efficiencies for office buildings measured by Li and Harrison (1990) averaged 0.82. Because aerosol strong acidity is singularly associated with the sulfate component and with sizes in the  $0.1\text{-}0.5\text{ }\mu\text{m}$  range (Koutrakis et al., 1989), it follows that penetration of aerosol acidity is also very high. However, the effective infiltration depends upon chemical loss terms, since the physical losses from deposition (as for sulfate) are low.

Neutralization of acidic aerosol by ammonia appears to control the levels occurring indoors. Levels of indoor ammonia are much higher than those measured outdoors. Humans (and pets) are a principal source of ammonia in occupied spaces; breath and sweat are highly concentrated NH<sub>3</sub> sources. The use of ammonia-containing cleansers can also contribute in some settings. Hence, it is the presence of people and their activities which creates the ammonia-laden atmospheres indoors. The infiltrated acidic sulfate aerosols and high indoor ammonia levels have ample time for the neutralization reaction to go to completion. However, data from indoor studies (Brauer et al., 1991; Liang and Waldman, 1992) indicate the reaction rate occurs in the range of 15 to 90 min, far longer than laboratory data for pure components suggest (Huntzicker et al., 1980).

U.S. EPA recently began a program to characterize acidic aerosol exposures for metropolitan areas. In the spring of 1992, Harvard School of Public Health and Robert Wood Johnson started a multi-site field monitoring program in and around Philadelphia, using measurements for a network of ambient sites and indoor monitoring in homes, offices and schools. This paper provides a preliminary report on the measurements for acidic aerosols utilizing ADS during June-August of 1992 inside 15 different microenvironments (schools and youth centers).

**METHODS**

Acidic aerosol samplers were operated indoors at a set of public school and recreational buildings. The sites are described in Table 1; their locations are shown in Figure 1. The samplers were situated inside occupied rooms and operated for 12-h (8 am to 8 pm LDT). Three sites were monitored, Monday to Saturday, for 2 to 3 weeks at a time. For each interval, an outdoor sampler was operated on the roof (generally 6-10 m above ground level) at one of the three sites.

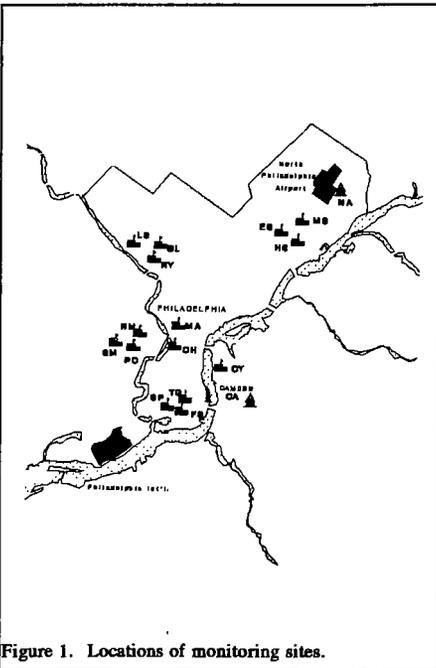


Figure 1. Locations of monitoring sites.

Table 1. Sites and Schedules for Summer 1992.

<b>SCHOOLS</b>	
<u>NO. PHILADELPHIA</u>	June 1 to 15
Lincoln Senior High School	HS
Austin Meehan Middle School	MS/MO <sup>a</sup>
Mayfair Elementary School	ES
<u>SO. PHILADELPHIA</u>	June 15 to 25
South Philadelphia High School	SP
John H. Taggart Middle School	TG/TO <sup>a</sup>
Francis S. Key Elementary School	FS
<b>RECREATION CENTERS and DAYCARES</b>	
<u>CENTRAL PHILA./CAMDEN</u>	July 6 to 25
Christian Street YMCA	CH
Marian Andersen Recreation Ctr.	MA/BO <sup>a</sup>
Camden YMCA (6/26-8/1)	CY/CO <sup>a</sup>
<u>W. PHILADELPHIA</u>	July 31 to Aug 13
Ronald MacDonald House	RM
St. Mary's Nursery School	SM
Penn Children's Center	PC/WP <sup>a</sup>
<u>ROXBOROUGH/NW PHILA.</u>	Aug 17 to Sept 1
Green Lane Nursery School	GL
Lyceum Nursery School	LS
Roxborough YMCA	RY/RO <sup>a</sup>
<b>AIR MONITORING STATION</b>	June 1 to Sept 15
Camden Lab - Daily 24-h	CA <sup>a</sup>

a. Outdoor samplers.

In addition, daily 24-h samples were collected at a Camden site throughout the entire summer study period. The Annular Denuder System (ADS) was used to collect aerosol along with gaseous components, using a preseparator cut at 2.5  $\mu\text{m}$ ad (Liang and Waldman, 1992). To estimate air exchange rates, a perfluorocarbon tracer system was used (Dietz et al., 1986); individual measurements were made with 24-h sampling periods.

## RESULTS

Results for aerosol acidity, sulfate and gaseous ammonia are shown in Figure 2. These data are the average concentrations for 12-h daytime measurements at the indoor sites during the 2-3 week sampling periods. Following each set of three indoor sites, the results for the proximal outdoor sites are shown. The indoor concentrations of sulfate were comparable to the outdoor levels. This pattern is seen in the daily data. Sulfate aerosol concentrations in the northeast U.S. are spatially homogeneous over a wider area (Waldman et al., 1991; Thurston et al., 1992; Liang and Waldman, 1993). The correlations among indoor sites were somewhat less than those among outdoor sites. Site-specific penetration efficiencies, while typically high, contributed more variability to the daily levels among indoor sites than the spatial gradients over the metropolitan area.

Ambient aerosol acidity was uncharacteristically low during this summer. Outdoor concentrations (12-h) averaged below 30 nmole  $\text{m}^{-3}$ , with peak values not exceeding 100 nmole  $\text{m}^{-3}$ . For data reported in nearby sites in New Jersey for a previous summer (1989), the average concentration (12-h) was 50, with maximum levels that reached 200 nmole  $\text{m}^{-3}$  (Liang and Waldman, 1992; 1993).

Indoor/outdoor ratios for  $\text{H}^+$  and  $\text{SO}_4^{2-}$  are given in Table 2. The indoor levels were, as expected, lower than outdoor concentrations. However, since there was little aerosol acidity available to drive indoor levels, it is difficult to interpret the patterns in neutralization. Indoor concentrations of ammonia and nitrous acid (HONO) were substantially higher than outdoor levels.

The indoor/outdoor (I/O) ratios for aerosol sulfate and acidity are shown in Figure 3. The patterns are consistent with previously reported results, indicating fine aerosol (sulfate) had  $\approx 80\%$  penetration efficiency. The I/O ratio for acidic aerosol were much more variable. At some locations, the results indicate effective neutralization of the particles that penetrate (e.g. TG, FS, CY(P1) and CH). For other sites, the acidic aerosol appears to have the same penetration efficiency as sulfate, indicating very little neutralization (CY(P1), CH(P1), and MA). It is likely that the relatively low acidity levels has biased some of these relationship, since neutralization kinetics may be lower at very low acidity levels.

Table 2 gives the air exchange rates (AER) measured for the indoors sites. The rates were generally lower when AC was used. Some high AER for AC buildings may have been due

**Table 2. Acid fraction and I/O ratios.**

Period	Site	H/SO <sub>4</sub>	NH <sub>3</sub> ppb	AER 1/h	Vent.
P1	HS	0.00	24	1.3-1.8	OW
	MS	0.06	10	0.7-0.8	AC
	ES	0.07	25	0.6-0.8	OW
P2	SP	0.13	14	1.2-2.4	OW
	TG	0.08	21	1.4-2.9	OW
	FS	0.24	15	1.0-6.0	OW
P3	CY	0.13	33	na	AC
	MA	0.25	33	na	OW
	CH	0.16	53	na	AC
P4	CY	0.02	42	8.5-11	AC
	MA	0.09	35	3.3-5.0	OW
	CH	0.03	37	0.9-3.2	AC
P5	RM	0.17	na	0.4-1.5	OW
	SM	0.06	na	0.6-0.8	AC
	PC	0.25	na	2.5-3.5	AC

Periods: P1: June 1-14; P2: June 15-28;  
P3: June 29-July 12; P4: July 13-26;  
P5: July 27-Aug 13.

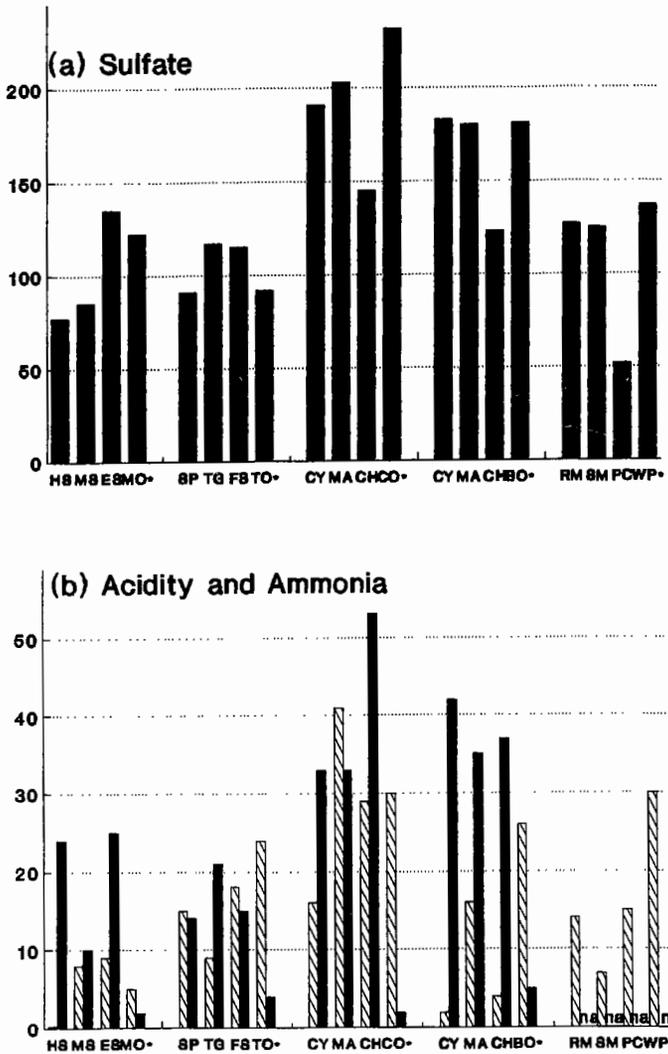


Figure 2. Average concentrations for (a) sulfate and (b) acidic aerosol for intervals P1 through P5.

to direct ventilation into the sampling area (e.g. CY and PC). The differences in aerosol penetration for buildings with air conditioning (AC) versus *windows-open* (WO) ventilation were not consistent, however.

**DISCUSSION**

Like most buildings, these schools and recreational centers allowed penetration of the ambient fine sulfate aerosol. Air conditioning did not seem to cause a consistent reduction in indoor levels of aerosol nor an elevation in ammonia. However, there were site-specific patterns in acidic aerosol neutralization.

Indoor ammonia (12-h daytime average) was in the 10-50 ppb range, while outdoor levels were  $\approx 2$  ppb. The rooms monitored were relatively large (100-300 m<sup>3</sup>). The source strength of ammonia can be calculated using a simple box model (Liang and Waldman, 1992):

$$E_a = R V C_i$$

where  $E_a$  is the emission rate ( $\mu\text{mole h}^{-1}$ ); R is the air exchange rate ( $\text{h}^{-1}$ ); V is the room volume ( $\text{m}^3$ ); and  $C_i$  is the indoor concentration ( $\mu\text{mole m}^{-3}$ ). Note: the conversion is  $1 \text{ ppb} \approx 0.04 \mu\text{mole m}^{-3}$ . For the parameters measured in the sites, the ammonia emissions are calculated to be in the range of 100-300  $\mu\text{mole h}^{-1}$ . Occupancy in the sampling rooms occurred for at least six of the 12-h interval, and 20 or more children were present. In their discussion section, Liang and Waldman estimate ammonia emission strengths as 8  $\mu\text{mole h}^{-1}$  from exhaled breath and as much as 150  $\mu\text{mole h}^{-1}$  from sweat, per adult.

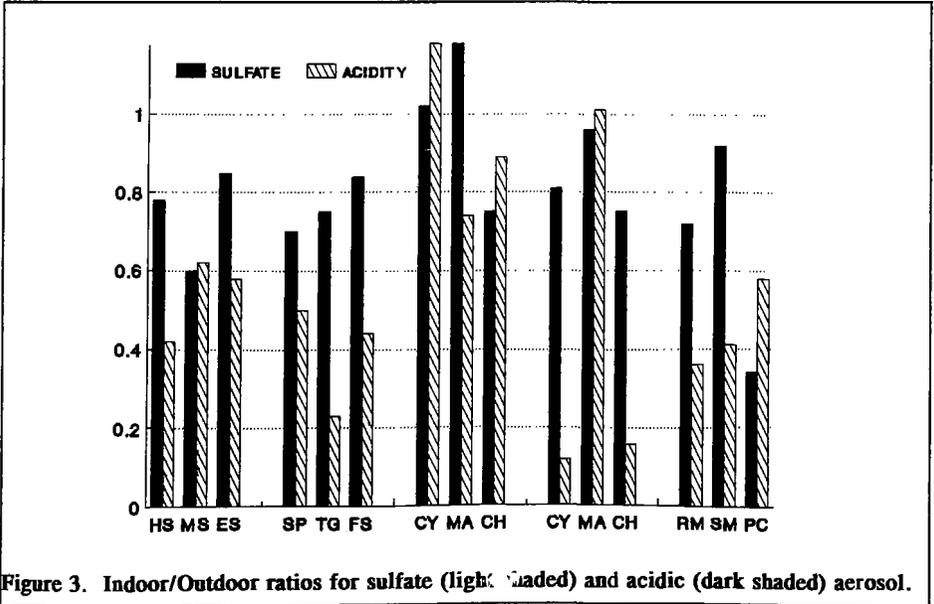


Figure 3. Indoor/Outdoor ratios for sulfate (light shaded) and acidic (dark shaded) aerosol.

## CONCLUSIONS

As in previous studies of aerosol acidity, the summer 1992 study in Philadelphia/Camden schools and recreational centers yielded indoor levels of  $H^+$  and  $SO_4^{2-}$  that were lower than outdoor concentrations, while indoor HONO and  $NH_3$  exceeded their levels outdoors. Air exchange rates were measured in the range 1-6  $h^{-1}$ . In some sites, neutralization was more than 50%; in others, the acidic aerosol was largely unneutralized. Notwithstanding the mode of ventilation (AC or open windows), the ammonia concentrations in occupied rooms were consistently high (30-50 ppb). However, the uncharacteristically low ambient concentrations for acidic aerosols obscured details about the ammonia neutralization patterns. The data will be used to assess whether the magnitude of children's exposures to acid aerosols pose a potential health risk and to investigate neutralization processes caused by indoor ammonia.

## ACKNOWLEDGEMENTS

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## SPANNING FROM REGIONAL TO MICROENVIRONMENTAL SCALES OF EXPOSURES TO ACID AEROSOLS

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### ABSTRACT

To predict human exposure to acid aerosols spanning from regional to microenvironmental scales is a challenging task. We have investigated spatial patterns of acid aerosols in two field studies (New Jersey and Atlanta) with sampling sites from 20 to 100 km apart. In both studies, acidity was found homogeneously distributed among sampling sites during the daytime. The consistency of this finding indicates that outdoor exposure to acid aerosols throughout these regions could be estimated with one central monitoring station during the daytime. Sulfate was found homogeneously distributed among sampling sites for both studies and both daytime and nighttime. The difference in spatial patterns between sulfate and acidity indicates sulfate may not be a proper surrogate for acid aerosols. In addition, we conducted measurements inside homes and institutions in each study. The average indoor/outdoor ratios of acid ranged from 0.13 (air conditioned) to 0.73 (open window) and were not correlated with outdoor values in most of the cases. Indoor ammonia levels were approximate 4 to 12 times higher than outdoor levels. The impact of ammonia on acid aerosols was variable; however, a qualitative inverse relationship between ammonia and acid/sulfate ratio was evident from site to site.

Correlation and ANOVA analyses are proposed to evaluate spatial patterns of pollutants within sampling programs. This methodology can be used to standardize the evaluation from different research studies and assist meaningful comparison and interpretation of spatial results.

### INTRODUCTION

Acid aerosols have been recognized as one of the regional pollutants that cause respiratory health effects. Although many studies have been conducted to measure the ambient levels of acid aerosols, only limited research has focused on regional spatial variations and relationships among sampling sites. Acidity and sulfate levels are found highly correlated ( $r^2 > 0.90$ ) between sites 10-35 km of a rural community<sup>1,2</sup> but correlation strength decreases for distances of 160 to 400 km apart ( $r^2 \approx 0.5$ )<sup>3</sup>. The spatial correlation among sampling sites is influenced to different extents by neutralization with ambient ammonia<sup>4</sup>, direct emission of acid aerosols, precursors presented in the atmosphere, and photo-chemical conditions<sup>5</sup>. These ongoing processes affect the spatial patterns of acid aerosols, which determine the exposure levels of populations on a community scale.

We conducted two regional sampling programs concurrent with indoor measurements: in New Jersey (suburban area during the summer of 1989) and in Atlanta (metropolitan area during the summer of 1990). Our primary objectives herein are to examine the representativeness of outdoor sampling stations for ambient acid aerosol levels and to propose a methodology to evaluate spatial patterns of air pollutants. This can be seen as an exploratory approach; the specific results and methodology might be used to compare other studies in a consistent format. In addition, the understanding of spatial patterns of acid aerosols will help to identify the location of potential exposures and assist regulatory agencies in setting up control and monitoring strategies.

## METHODS

In the New Jersey study, daily 12-h samples were collected from mid-June to early August 1989. There were three outdoor sampling stations located in suburban to rural areas. The stations were deployed in northern (CH), central (RC) and southern (ST) New Jersey (Figure 1, left). The distance from CH to RC is approximately 60 km, while RC to ST is approximately 110 km. Twice daily samples were collected every day at RC site, while CH and ST sites' samplers were operated on an every other day schedule. Three indoor sites were selected within 5 km of the RC site, and daily 12-h daytime samples were collected. The Atlanta study had a similar spatial and sampling design except all outdoor locations were in an metropolitan area (Figure 1, right). Twice daily 12-h samples were collected at the outdoor sites (except daytime only at HO) for 28 days in August. Two indoor sites were selected within the metropolitan area, and daily 12-h daytime samples were collected. Annular Denuder System (ADS) samplers were used to collect fine acid aerosols ( $<2.5 \mu\text{m}$ ,  $\text{H}^+$ ,  $\text{SO}_4^-$ ,  $\text{NH}_4^+$ ) and relevant gaseous components ( $\text{SO}_2$ ,  $\text{HNO}_2$ ,  $\text{HNO}_3$ ,  $\text{NH}_3$ )<sup>6,7,8</sup>.

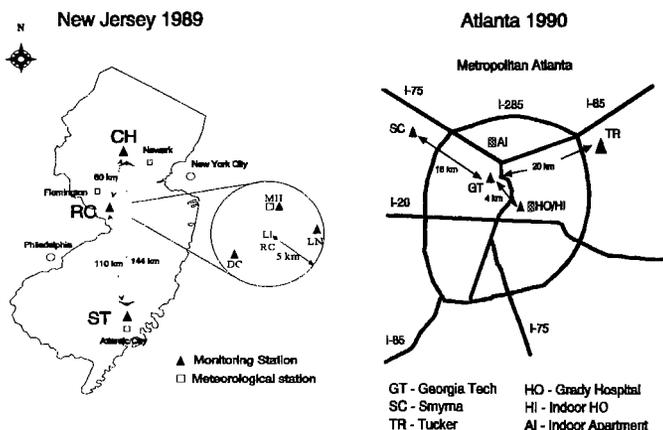


Figure 1. Spatial plans of outdoor and indoor sampling locations.

With this sampling design, "the representativeness of central monitoring station over the study area" is being tested by the following considerations. First, the pollutant of concern is homogeneously distributed among sampling sites. Second, the uncertainty associated with concurrent collected samples is small. We define the representativeness of the central monitoring station as satisfying the following criteria at the confidence level of  $\alpha=0.05$ : (a) measurements at one location are "correlated" with measurements acquired at adjacent monitoring stations, and (b) the central monitoring station will have the "same mean" as the adjacent monitoring stations over a period of time. The approach methodology is illustrated in Figure 2.

**Correlation analysis.** Acidity and relevant species are analyzed for correlation among sampling sites. Species with non-significant correlation ( $\alpha=0.05$ ) are characterized as spatially non-homogeneously distributed among sampling sites. Species with significant correlation will be analyzed further.

**ANOVA analysis with "Repeated Measurement Design<sup>9</sup>".** Taking each day/night measurement as an independent measurement and local influence as treatment (site effects), the mean values of the sites are examined through analysis of variance (ANOVA) at  $\alpha=0.05$ . Certain data transformations may be required to improve the data distribution toward a normal distribution. Chemical species which failed in

the ANOVA analysis are characterized as spatially non-homogeneously distributed among sampling sites. Chemical species passing both correlation and ANOVA tests are characterized as spatially homogeneous among sampling sites, and the measurements at central location are considered to be representative over the study area. In other words, one central monitoring station can be used to represent or estimate air quality and human exposure over a larger scale.

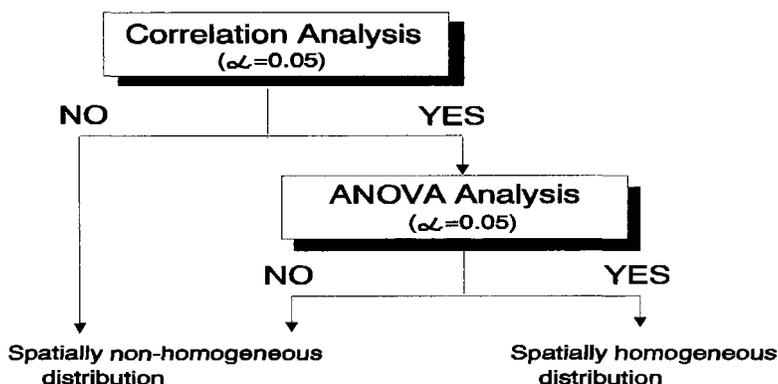


Figure 2. Methodology for spatial evaluation.

## RESULTS

The correlation of chemical species among sampling sites for both studies is listed in Table 1. Acidity was found correlated among sampling sites for both studies during the daytime. At night, acidity was correlated only in Atlanta study. Sulfate was found correlated in both studies for both daytime and nighttime periods. The rest of the chemical species were found not significantly correlated at the level  $\alpha = 0.05$ . The ANOVA analyses of mean values at each sampling site are tabulated in Table 2 and 3. When combining the correlation and ANOVA analyses of means, acidity and sulfate were homogeneously distributed among sampling site during the daytime periods for both studies. During the nighttime periods, sulfate was the only chemical specie homogeneously distributed among sampling sites for both studies.

In general, the spatial patterns observed between New Jersey study and Atlanta study were similar. Acidity was homogeneously distributed during the daytime while sulfates were homogeneously distributed for both daytime and nighttime. Chemical species such as  $\text{HNO}_2$ ,  $\text{HNO}_3$ , and  $\text{NH}_3$  were spatially non-homogeneously distributed among sampling sites. Nevertheless, ANOVA analyses in Table 2 & 3 indicated there were differences in spatial patterns between two studies. For instance, the mean levels of  $\text{SO}_2$  were found not significant different among sampling sites for both daytime and nighttime periods in New Jersey study while significant different among sampling sites in metropolitan Atlanta. This indicated there were more local factors which altered the  $\text{SO}_2$  levels in the metropolitan area.

There were no obvious sources of acid aerosols in any of the indoor environments in these studies. The indoor/outdoor ratios of acid ranged from 0.13 (air conditioned type of settings) to 0.73 (open window type of settings). In most cases, acidity was not significantly correlated with corresponding outdoor levels for the time series measured. Aerosol sulfate demonstrated a strong penetration capability for all indoor measurements. The indoor/outdoor ratios ranged from 0.74 (air conditioned settings) to 1.04 (open window settings), and high correlations were evident between indoor

and outdoor concentrations. The presence of indoor sources of ammonia was obvious. Ammonia levels were at least 4 to 12 times higher than corresponding outdoor levels.

## DISCUSSIONS

It should be noted that the results of similar spatial studies may vary due to the following factors. First, the representativeness of outdoor monitoring station is evaluated through correlation and ANOVA analysis with  $\alpha=0.05$ . The selection of a lower  $\alpha$  value would be a more stringent test. Spatial differences in concentrations would be more likely be found. Second, the number and selection criteria of sampling sites are important factors in determining the spatial patterns. A higher number of sampling sites means a greater chance these sampling sites would identify the local differences in concentrations.

Ammonia is known as the most abundant alkaline gas in the atmosphere, and the amount present is associated with various human activities. The detailed kinetic mechanism of ambient acid aerosols neutralized by ammonia is not entirely clear, and the relationships found for individual sample are not readily predicted. However, we notice a consistent qualitative relationship between average ammonia levels and average acid ratios ( $H^+/SO_4^{2-}$ ) at different locations (Figure 3). This qualitative relationship, at least, may assist to locate the potential exposure area for health studies.

## CONCLUSIONS

The correlation and ANOVA analyses are proposed to evaluate spatial patterns of pollutants with concurrent sampling programs. This methodology can be used to standardize the evaluation from different research studies and assist meaningful comparison and interpretation of spatial results.

Acidity was found homogeneously distributed among sampling sites for both studies during the daytime but not for nighttime periods. In the other word, the central outdoor monitoring stations could be used to represent the concentration/exposure over a larger scales during the daytime. This is important especially since most of the episodic exposure occurred in the daytime. Sulfate was found homogeneously distributed among sampling sites for both studies and both daytime and nighttime. The difference in spatial pattern between sulfate and acidity indicated sulfate may not be a proper surrogate for acid aerosols. Pollutant species such as  $HNO_2$ ,  $HNO_3$ ,  $SO_2$  and  $NH_3$  were found not homogeneously distributed among sampling sites for both studies and both sampling periods.

## ACKNOWLEDGMENTS

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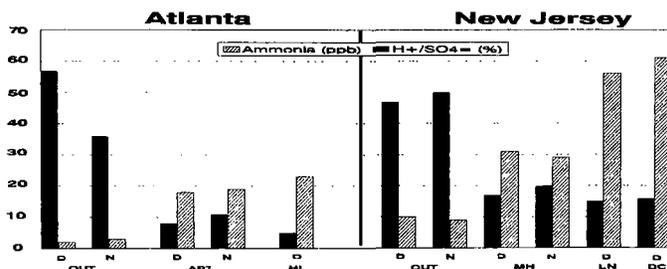


Figure 3. Average ammonia versus acid ratio ( $H^+/SO_4^-$ ).

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Table 1. Correlation analysis with  $\alpha=0.05$  among three sampling sites.

Component	New Jersey 1989		Atlanta 1990	
	AM	PM	AM	PM
H+	Correlated	X	Correlated	Correlated
SO <sub>4</sub> <sup>=</sup>	Correlated	Correlated	Correlated	Correlated
SO <sub>2</sub>	X	X	X	X
HNO <sub>3</sub>	X	X	X	X
HNO <sub>2</sub>	X	X	X	X
NH <sub>3</sub>	X	X	X	X

X: Non-significant correlated at  $\alpha=0.05$ .

**Table 2. Results of spatial variation among outdoor sampling sites. (New Jersey 1989)**

Species/Parameters	Results	Locations (mean conc. in neq/m <sup>3</sup> )		
<b>AM</b>				
Acidity	NS	ST(59)	CH(52)	RC(44)
SO <sub>4</sub> <sup>=</sup>	NS	RC(117)	CH(100)	ST(91)
HNO <sub>2</sub>	Significant	RC(29)	CH(26)	ST(17)
HNO <sub>3</sub>	Significant	RC(79)	ST(56)	CH(47)
SO <sub>2</sub>	NS	RC(170)	ST(158)	CH(132)
NH <sub>3</sub>	Significant	CH(117)	RC(105)	ST(63)
<b>PM</b>				
Acidity	NS	CH(41)	ST(38)	RC(23)
SO <sub>4</sub> <sup>=</sup>	NS	RC(87)	CH(74)	ST(60)
HNO <sub>2</sub>	NS	RC(47)	CH(38)	ST(35)
HNO <sub>3</sub>	NS	CH(20)	ST(19)	RC(17)
SO <sub>2</sub>	NS	RC(114)	CH(107)	ST(74)
NH <sub>3</sub>	Significant	RC(119)	CH(116)	ST(70)

Note: Locations connected with solid underline are not significantly different in concentration from each other ( $\alpha=0.05$ ). NS: Non Significant different.

**Table 3. Results of spatial variation among outdoor sampling sites (Atlanta 1990).**

Species/Parameters	Results	Location (mean conc. in neq/m <sup>3</sup> )			
<b>AM</b>					
Acidity	NS	GT(87)	SC(83)	TR(81)	HO(77)
SO <sub>4</sub> <sup>=</sup>	NS	GT(245)	HO(223)	TR(223)	SC(204)
HNO <sub>2</sub>	Significant	HO(158)	SC(129)	GT(126)	TR(102)
HNO <sub>3</sub>	Significant	HO(107)	GT(105)	SC(98)	TR(59)
SO <sub>2</sub>	Significant	HO(437)	GT(417)	SC(269)	TR(170)
NH <sub>3</sub>	Significant	HO(93)	GT(62)	TR(52)	SC(51)
<b>PM</b>					
Acidity	Significant	SC(52)	TR(47)	GT(35)	
SO <sub>4</sub> <sup>=</sup>	NS	GT(218)	SC(213)	TR(204)	
HNO <sub>2</sub>	NS	TR(109)	SC(104)	GT(104)	
HNO <sub>3</sub>	Significant	TR(62)	GT(38)	SC(25)	
SO <sub>2</sub>	Significant	GT(309)	SC(219)	TR(166)	
NH <sub>3</sub>	Significant	GT(78)	SC(56)	TR(37)	

*Session 21*

*Acid Aerosol*

*Field Study Results*

## Measurement of Acidic Aerosol Species in Eastern Europe

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### ABSTRACT

Ambient measurements of acid aerosols were made for approximately one and a half years in Erfurt, Germany and Sokolov, Czechoslovakia. In both locations, the burning of high sulfur coal is the primary source of ambient air pollution. In Erfurt, coal-fired power plants and residential coal burning are the major contributors, while major sources in Sokolov are several power plants and a coal gasification plant. 24 hour average measurements were made for PM<sub>10</sub>, as well as fine particle ( $d_a < 2.5 \mu\text{m}$ ) H<sup>+</sup> and SO<sub>4</sub><sup>2-</sup> for the entire study. Additionally, separate day and night measurements of fine particle H<sup>+</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> and the gases, SO<sub>2</sub>, HNO<sub>3</sub>, HONO and NH<sub>3</sub> were collected over a 7 month (late winter-summer) period with additional measurements during pollution episodes the following winter.

In both communities, 24-hour SO<sub>2</sub> (mean concentrations of 20 ppb, with peak levels of >150 ppb) and PM<sub>10</sub> (mean concentration >50 μg m<sup>-3</sup>) concentrations were quite high. However, aerosol SO<sub>4</sub><sup>2-</sup> concentrations (mean concentration of approximately 100 nmol m<sup>-3</sup>) were not as great as expected given the high SO<sub>2</sub> concentrations and acidity was very low (mean concentration of <20 nmol m<sup>-3</sup>, with peak levels of only 150 nmol<sup>-3</sup>). Low acidity is likely to be the result of NH<sub>3</sub> neutralization and slow conversion of SO<sub>2</sub> to SO<sub>4</sub><sup>2-</sup>. Measurements indicate the presence of neutralized ammonium sulfate species as well as NH<sub>4</sub>NO<sub>3</sub>. We use our substantial database of acid aerosol measurements in North America as well as historical data from London in comparisons with our observations of very low levels of aerosol acidity in these Eastern European measurements. Additionally, we compare characteristics of the chemical composition of these Eastern European winter atmospheres to summer episodes in the eastern U.S and Canada.

### INTRODUCTION

With the end of Communist rule in Eastern Europe and the new access to information, it has become clear that many countries suffered severe environmental neglect. As these countries struggle with the transition to free market economies there is an urgent need to examine and prioritize environmental health concerns so that control measures can be taken. As part of this effort a major air pollution epidemiology study was undertaken in the former East Germany and in the Czech Republic. As part of this study, ambient air measurements of PM<sub>10</sub>, acidic aerosols and gas species and NH<sub>3</sub> were conducted for approximately 1.5 years at two sites. This monitoring effort provided a unique opportunity to examine levels of acidic aerosol species in environments that were directly impacted by both local and regional sources of high sulfur "brown coal." Monitoring was specifically focused on winter inversions during which pollutant concentrations were expected to be highest. This situation was thought to resemble historical episode situations encountered 30-40 year ago in London, England, the Meuse Valley in

Belgium and Donora PA in which increased daily mortality has been associated with air pollution exposure<sup>1-3</sup>. Although only limited measurements were made it has been argued that the causative agent in these episodes was aerosol acidity. Here we report measurements of acidic aerosols and gases from an urban location in the former East Germany and from a smaller industrial town in the Czech Republic. Comparisons are made between these results and those collected recently in the U.S. and Canada.

## METHODS

### Site Characterization

Two cities were selected for air monitoring, Erfurt (ERF), in the former East Germany and Sokolov (SOK) in the Czech Republic. Both Erfurt and Sokolov were reported to be subject to winter inversions which resulted in poor ambient air quality (high TSP and SO<sub>2</sub> concentrations) and reduced visibility. Erfurt (population approximately 200,000) is located northwest of Frankfurt, approximately 100 km east of the former east-west border and is a regional center of commerce. The city has a large older central area where the primary heating source is individual coal furnaces. The outer areas of the city contain large apartment complexes with steam heat supplied by a large coal burning power plant located several km east of the city center. Erfurt is situated on a flat plain bordered by a ridge on the south end of the city. The sampling site was located less than 5 km from the town center, 15 m from the nearest structure and 30 m from the nearest major road. Sampler inlets were located approximately 2m from ground level. Sokolov (population approximately 60,000) is an industrial town located in the coal-mining region of the Czech Republic, 100 km east of the German-Czech border. There are several power plants and large industrial complexes in the region, in addition to a coal gasification plant. Sokolov is located in a valley surrounded by low hills. The sampling site was located on the terrace of a two-story building approximately 2 km from the central district. Sampler inlets were located 2 m above the terrace surface.

### Sampling and Analysis

Particulate acidity (PM<sub>2.5</sub>) and PM<sub>10</sub> samples were collected with the Harvard Impactor (with the addition of a citric-acid coated honeycomb denuder for acidity sampling)<sup>4,5</sup>. The Harvard-EPA Annular Denuder System (HEADS) was used for measurements of gaseous species during some portions of the study. Sampling and analysis procedures are reported in detail elsewhere<sup>6,7</sup>. Daily or every second day 24-hour samples of fine particulate ( $d_a < 2.5 \mu\text{m}$ ) H<sup>+</sup> and SO<sub>4</sub><sup>2-</sup> were collected from December 1990 - June 1992 and 24-hour PM<sub>10</sub> samples were collected February 1991 - June 1992. Annular denuder measurements were made twice daily February 1991 - September 1991 and during episode periods from October 1991 - April 1992. Detection limits for 12-hour denuder measurements were 6.2 ppb, 1.8 ppb, 16 nmol m<sup>-3</sup>, 24 nmol m<sup>-3</sup>, 32 nmol m<sup>-3</sup> and 5.6 nmol m<sup>-3</sup>. for SO<sub>2</sub>, NH<sub>3</sub>, H<sup>+</sup>, SO<sub>4</sub><sup>2-</sup>, NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup>, respectively. The detection limit for PM<sub>10</sub> was 9  $\mu\text{g m}^{-3}$ . while the Harvard Impactor 24-hour detection limits were 8 and 15 nmol m<sup>-3</sup> for H<sup>+</sup> and SO<sub>4</sub><sup>2-</sup>, respectively.

## RESULTS AND DISCUSSION

Summary statistics are presented in Table 1. Aerosol acidity was low in both sites. Figure 1 compares the annual means measured in Erfurt and Sokolov to those measured in 22 North American communities as part of a major epidemiological study. The eastern European sites report aerosol acidity concentrations which are at the low end of the observations in North America. While concentrations of PM<sub>10</sub> and SO<sub>2</sub> in Erfurt and Sokolov were significantly higher in the winter, aerosol acidity was slightly higher in the summer at both sites. This contrasts with observations from North America in which summer acidity levels are much greater than those measured in the winter. Low aerosol acidity may result from low SO<sub>4</sub><sup>2-</sup> production or from neutralization of acidic sulfate species by ambient NH<sub>3</sub>. Although acid aerosol levels were very low, comparisons to the North American database of SO<sub>4</sub><sup>2-</sup> measurements (Figure 2) indicates that the eastern European sites presented much higher concentrations. A plausible cause for the observations of low aerosol acidity and high SO<sub>4</sub><sup>2-</sup> concentrations is the elevated levels of ambient NH<sub>3</sub> (Table 1) at Sokolov and Erfurt. Although the record of NH<sub>3</sub>

concentrations is less complete, mean concentrations during the sampling periods were consistently high (> 2 ppb) throughout the year. Annual averages measured in North American communities are typically below 1.5 ppb, with only the rural California sites reporting annual means above 2 ppb.

PM<sub>10</sub> and SO<sub>2</sub> concentrations at both eastern European sites were quite high and were well above concentrations observed in the North American communities (Figure 3-4). Concentrations were higher during the winter than in the summer which is consistent with the occurrence of winter inversions and increased coal burning (particularly in Erfurt) for residential heating.

The meteorological conditions of local winter inversions suggests that SO<sub>2</sub> and consequently SO<sub>4</sub><sup>2-</sup> ("potential acidity") concentrations and NH<sub>3</sub> will peak at the same times, limiting the opportunity for acidic particles to avoid neutralization. In North American summer episodes it is believed that convective mixing replaces stagnant surface-level air (high ammonia content) with acid-laden air that has been transported above inversion layers where it is protected from neutralization<sup>8,9</sup>. The situation in eastern Europe also differs in terms of the proximity of the sources - with local sources emitting SO<sub>2</sub> below inversion layer heights and therefore in close proximity to ammonia sources. Since the acidic and basic air masses are not separated there is ample opportunity for neutralization to occur.

Further, the SO<sub>2</sub> conversion reactions are expected to differ between eastern Europe and North America where photochemical reactions predominate. In North America, emissions are typically above the height of inversion layers under conditions of low particle concentrations, facilitating transport of gaseous species. Transport at high elevations provides adequate time for conversion while being protected from neutralization by surface level sources of NH<sub>3</sub>. The predominant conversion mechanism in North America is photochemical, based on the reaction of hydroxyl radical with SO<sub>2</sub> in the presence of water. In eastern Europe, where winter inversions reduce the impact of photochemistry, heterogeneous reactions are expected to predominate. For example, SO<sub>2</sub> may be absorbed on particle surfaces and catalytically (by transition metals for example) oxidized to sulfuric acid. An additional pathway involves the diffusion of SO<sub>2</sub> into a liquid droplet where internal oxidation (by H<sub>2</sub>O<sub>2</sub> for example) produces sulfuric acid. This diffusion is controlled by the amount of NH<sub>3</sub> in the droplet such that any sulfuric acid produced will be immediately neutralized in the basic environment. As the droplet becomes more acidic further diffusion of SO<sub>2</sub> into the droplet is limited. This slow conversion mechanism is likely to be important for moist environments with high particle concentrations such as those in Sokolov and Erfurt. This aqueous phase oxidation mechanism may explain our observations of lower than expected sulfate levels at a given SO<sub>2</sub> concentration as well as the high levels of NH<sub>4</sub><sup>+</sup> ion observed (mean concentrations >230 nmol m<sup>-3</sup>). In the winter inversion setting concentrations of oxidizing species may be quite low and conversion of SO<sub>2</sub> may be quite limited. Conversion rates are highest (10-40% per hour) for metal-catalyzed reactions, although there is considerable variability depending upon the pH of the droplet as well as the presence of inhibitors. Homogeneous gas phase reactions occur at rates of 0.3-2% per hour, while aqueous phase oxidation is much slower (0.2% per hour).

The extent of SO<sub>2</sub> conversion may be estimated by the  $[\text{SO}_4^{2-} / \text{SO}_4^{2-} + \text{SO}_2]$  ratio. Much like the North American situation, the ratios in Erfurt and Sokolov were lower in the winter than in the summer. Ratios were typically below 0.25 in the winter, and reached peaks of 0.6 or higher in the summer. While these ratios suggest considerable conversion in the summer, SO<sub>2</sub> concentrations were low during this period. In the winter, when SO<sub>2</sub> concentrations are elevated,  $[\text{SO}_4^{2-} / \text{SO}_4^{2-} + \text{SO}_2]$  ratios were below those seen in summer acidic atmospheres in North America (mean ratios of 0.4-0.6) (Keeler, Keeler), suggesting the impact of slower SO<sub>4</sub><sup>2-</sup> production processes.

Measurements from other coal-burning areas are presented in Table 1 for comparison. Waldman and colleagues collected a limited number of measurements in Wuhan, China a region which may be

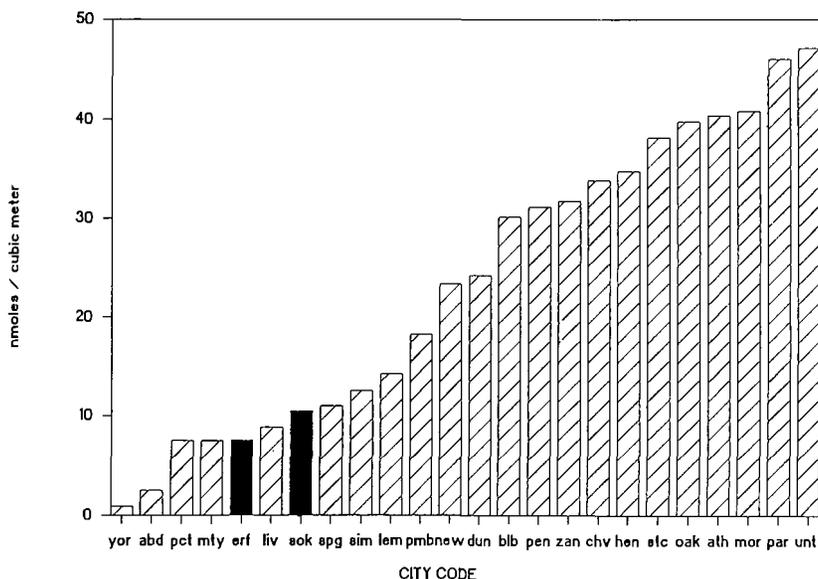
expected to be similar to the eastern European sites in that soft coal combustion produces elevated concentrations of particulate matter and SO<sub>2</sub>. The measurements of Waldman and colleagues were collected in the winter under similar conditions (overcast, cold, high relative humidity) to those observed in eastern Europe during the winter. While we measured higher peak levels of aerosol acidity than reported by Waldman, et al. this is likely due to the longer period of sampling. In both situations the levels of aerosol acidity were surprisingly low, given the high measured concentrations of SO<sub>2</sub> and PM<sub>10</sub>. Historical measurements from London were much higher than any present measurements. That SO<sub>4</sub><sup>2-</sup> levels were somewhat higher in Wuhan, than in Erfurt or Sokolov is interesting given the much higher SO<sub>2</sub> levels measured in Erfurt and Sokolov. SO<sub>2</sub> levels in Erfurt and Sokolov, although well below those measured in London were significantly higher than those measured in China. This indicates that conversion of SO<sub>2</sub> to sulfate was relatively low in the eastern European sites. In contrast the Wuhan environment may have presented more complete conversion, but acidity was controlled by neutralization. PM<sub>10</sub> concentrations were similar to concentrations measured in Wuhan. Although these comparisons are limited, they suggest that the conditions encountered in Erfurt and Sokolov may be typical of regions in which high sulfur coal is burned during the winter. In such situations, although PM<sub>10</sub> and SO<sub>2</sub> levels may be much greater than concentrations observed in North America, aerosol acidity levels are very low.

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**Table 1. Summary statistics of ambient concentrations measured in Sokolov and Erfurt and comparisons to measurements in China<sup>10</sup> and historical measurements in London<sup>1</sup>.**

Aerosol Acidity (nmol m <sup>-3</sup> )	Mean	Peak
Sokolov	10	166
Erfurt	8	156
Wuhan, China	14	50
London	133	2735
<b>SO<sub>4</sub><sup>2-</sup> (nmol m<sup>-3</sup>)</b>		
Sokolov	100	379
Erfurt	115	772
Wuhan, China	525	980
<b>NH<sub>3</sub> (ppb)</b>		
Sokolov	3.8	34
Erfurt	2.4	20
<b>SO<sub>2</sub> (ppb)</b>		
Sokolov	20	227
Erfurt	23	274
Wuhan, China	16	28
London	90	462
<b>PM<sub>10</sub> (µg m<sup>-3</sup>)</b>		
Sokolov	59	247
Erfurt	66	269
Wuhan, China		350



**Figure 1. Mean concentrations of aerosol strong acidity (nmol m<sup>-3</sup>) measured in Sokolov (SOK), Erfurt (ERF) and in 22 communities in the U.S. and Canada.**

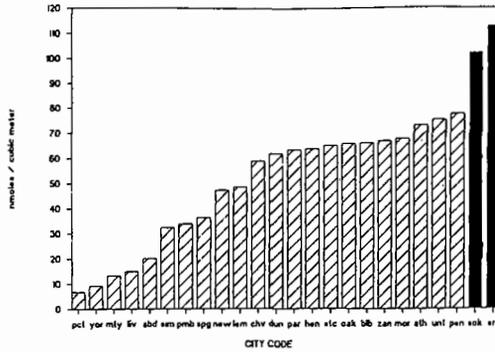


Figure 2. Mean concentrations of aerosol  $\text{SO}_4^{2-}$  ( $\text{nmol m}^{-3}$ ) measured in Sokolov (SOK), Erfurt (ERF) and in 22 communities in the U.S. and Canada.

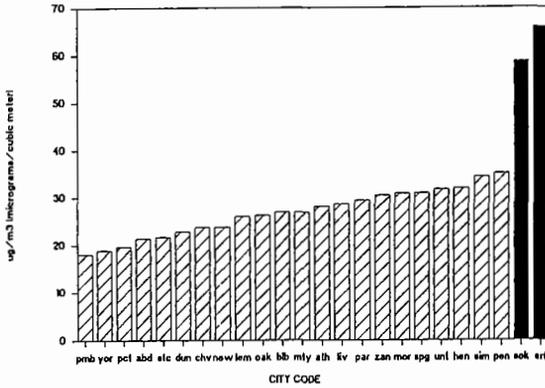


Figure 3. Mean concentrations of  $\text{PM}_{10}$  ( $\mu\text{g m}^{-3}$ ) measured in Sokolov (SOK), Erfurt (ERF) and in 22 communities in the U.S. and Canada.

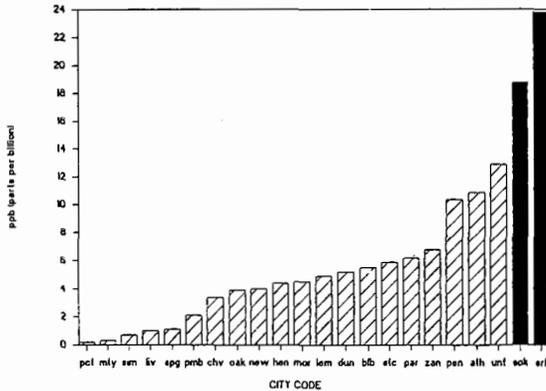


Figure 4. Mean concentrations of  $\text{SO}_2$  (ppb) measured in Sokolov (SOK), Erfurt (ERF) and in 22 communities in the U.S. and Canada.

# ACID AEROSOL MEASUREMENTS IN EASTERN CANADA

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## ABSTRACT

Measurements of fine aerosol strong acidity were collected during 1988-1991 at various Canadian locations as part of the Harvard School of Public Health and Health and Welfare Canada 24-Community Study<sup>1</sup>. Measurement activities have continued since that time as part of the Canadian Acid Aerosol Measurement Program (CAAMP). Currently 7 sites in eastern Canada are in operation. Filterpack, denuder and dichotomous sampler or impactor measurements are being collected daily during May-September and every third day during the rest of the year. The details of the monitoring activities and preliminary results from 1992 are discussed in this paper.

## INTRODUCTION

Over the past 10 to 15 years a significant amount of research has focused on the acid deposition issue. Knowledge of the sources of acidifying pollutants and the atmospheric processes affecting their fate has improved substantially as has information on the temporal and spatial variability in their deposition. In general, more emphasis has been placed on monitoring deposition rates due to concerns over ecological effects. Consequently, less attention has been paid to the impact of acidic pollutants while still in the atmosphere. In this form they have the potential to adversely affect human health and to reduce visibility. These issues are currently receiving more attention in North America.

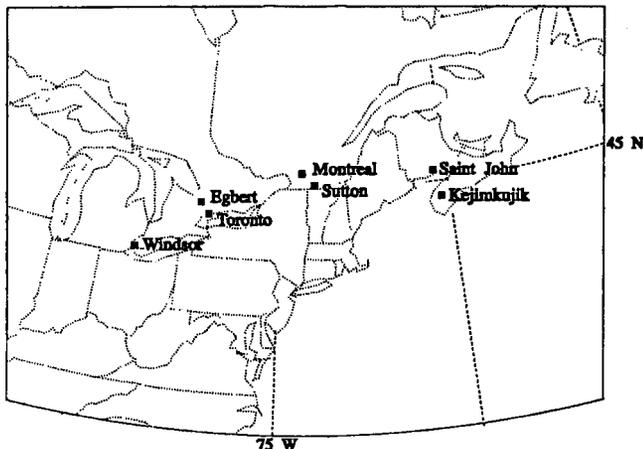
The Canadian Acid Aerosol Measurement Program (CAAMP), which formally started in 1992, aims to assist in the study of the health effects of acid rain related pollutants by meeting each of the following objectives:

1. Collect data, of known quality, on the acidity levels and fraction of aerosol mass in the fine and coarse mode at multiple Canadian locations.
2. Determine annual and seasonal averages, peak levels (12-24 hr) and temporal variability of aerosol acidity and fine (PM<sub>2.5</sub>) and coarse (PM<sub>10</sub>) masses.
3. Estimate the acid aerosol exposure of the Canadian population.
  - to assess the significance of the results of ongoing health effects research in a Canadian context
  - insure that the data are appropriate for incorporation in future health studies.

In this paper we describe the details of the sampling activities and present some of the results from the 1992 measurements.

## METHODS

At two Canadian Air and Precipitation Monitoring (CAPMoN) sites (Egbert, Ont and Sutton, Que) and one Ontario Ministry of the Environment site (Windsor) acid aerosol measurement equipment have been operating since June 1991 or before. During May, June and July of 1992 measurement activities at four new locations were initiated. All current measurement sites are shown in Figure 1. The operation of sites in urban areas reflects the interest in estimating the human exposure to acidic aerosols. Concentrations measured at rural sites are expected to be a better indication of the concentrations within larger, regional-scale air masses (i.e. the direct effects of urbanization are assumed to be small) thereby providing information on the spatial distribution of the aerosols. The current rural sites are in close proximity to the urban sites. This configuration will provide information on the amount of variability in



**Figure 1** The location of the Canadian Acid Aerosol Measurement Program (CAAMP) monitoring sites during 1992-93.

concentrations over relatively small distances and it may be possible to assess the effect of urban areas on aerosol acidity.

The main features examined by CAAMP are:

- The strong acidity of the fine fraction aerosols.
- The fraction of mass in the fine and coarse modes.
- The concentrations of the major inorganic aerosol constituents (ions and metals).
- Ambient  $\text{HNO}_3$  concentrations.

In Table 1 the various measurement parameters that are being collected at each site are listed. Four different sampling apparatus are being used to take these measurements. Both annular denuder systems (single and double denuder) and the fine and coarse mass particle sampling units (Air Diagnostics and Engineering 10 l  $\text{min}^{-1}$  10 and 2.5  $\mu\text{m}$  cut size inertial impactors) rely on a MKS 1159B-20,000SV mass flow controller, calibrated for 1 atm and 0° C, to regulate the flow rate. The flow rate during the 24 hour sampling duration is 10 l  $\text{min}^{-1}$ . The dichotomous samplers rely on their own pump and flow controller systems which maintain a total flow rate of approximately 16.7 l  $\text{min}^{-1}$ .

The supplies necessary to collect one week of samples and one blank (i.e. filterpacks, filters, impactor plates and denuders) are shipped to each site and stored at room temperature (~22° C). After all the supplies in a shipment have been used they are shipped back to the laboratory. Filterpacks are shipped and stored on site in sealed plastic bags and are only removed during the sampling period. Similarly denuders are kept capped except during sampling. The filterpacks are loaded with a Gelman Zeflour, supported PTFE, 2 $\mu\text{m}$  pore size Teflon filter which is situated immediately downstream of the denuders, followed by a nylon filter (Gelman Nylasorb) and a citric acid coated Whatman 41 filter. The Teflon filters collect the fine particles and the citric acid coated filters capture  $\text{NH}_3$  resulting from the

**Table 1** Summary of the particulate and gaseous species measured at the Canadian Acid Aerosol Measurement Program sites. Type of equipment used and the frequency of the the 24 hour measurements are also indicated.

SITE	Particulate	Gas	Frequency	Equipment
Windsor,	H <sup>+</sup> , SO <sub>4</sub> <sup>2-</sup> , NH <sub>4</sub> <sup>+</sup> , NO <sub>3</sub> <sup>-</sup>	HNO <sub>3</sub> , SO <sub>2</sub> ,	daily / 1 in 3 (Oct.-Apr.)	3-stage filterpack / 2 denuders
Kejimikujik	PM2.5, PM10 trace elements	NH <sub>3</sub>	daily / 1 in 3 (Oct.-Apr.) 1 in 6	dichotomous sampler dichotomous sampler
Egbert,	H <sup>+</sup> , SO <sub>4</sub> <sup>2-</sup> , NH <sub>4</sub> <sup>+</sup> , NO <sub>3</sub> <sup>-</sup>	HNO <sub>3</sub> , SO <sub>2</sub> ,	daily / 1 in 3 (Oct.-Apr.)	3-stage filterpack / 2 denuders
Sutton	PM2.5, PM10 trace elements	NH <sub>3</sub>	daily / 1 in 3 (Oct.-Apr.) 1 in 6	Air Diagnostics Impactors Air Diagnostics Impactors
Toronto,	H <sup>+</sup> , SO <sub>4</sub> <sup>2-</sup> , NH <sub>4</sub> <sup>+</sup> , NO <sub>3</sub> <sup>-</sup>	HNO <sub>3</sub> , SO <sub>2</sub>	daily / 1 in 3 (Oct.-Apr.)	3-stage filterpack / 1 denuder
Montréal,	PM2.5, PM10		daily / 1 in 3 (Oct.-Apr.)	dichotomous sampler
Saint John	trace elements		1 in 6	dichotomous sampler

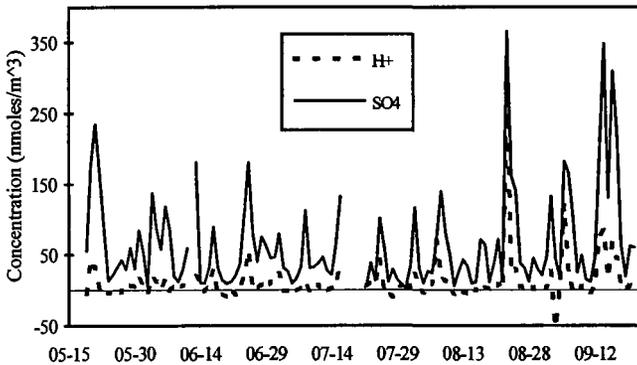
revoluitization of NH<sub>4</sub>NO<sub>3</sub> particles. In the double denuder system the nylon filter captures HNO<sub>3</sub> also resulting from the revoluitization of NH<sub>4</sub>NO<sub>3</sub> particles. Thus, an H<sup>+</sup> correction due to neutralization from NH<sub>3</sub> liberated from the NH<sub>4</sub>NO<sub>3</sub> particles is possible with the double denuder system. With the single denuder system the nylon filter provides a measure of both ambient HNO<sub>3</sub>, HNO<sub>3</sub> from NH<sub>4</sub>NHO<sub>3</sub> particles and also ambient SO<sub>2</sub>.

Samples were collected for 24 hour periods starting at 0800 EST. From May 1 or whenever sampling commenced to Sept. 21, 1992 measurements were taken every day. From Sept. 21, 1992 to the present samples have been collected every third day. All samples are analyzed for the species shown in Table 1 with the only exception being that elemental analysis using XRF is only carried out on every sixth sample, however, the remaining filters are being archived.

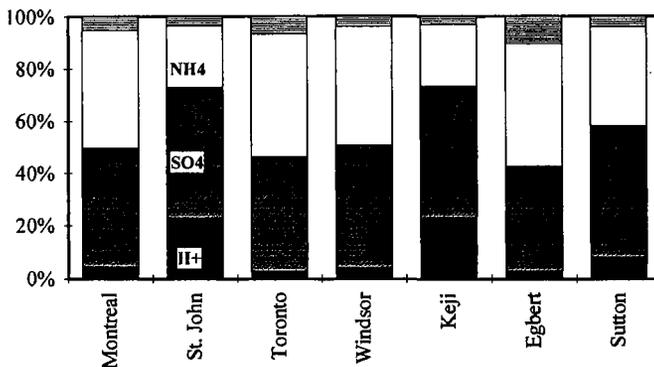
## RESULTS

All sites were operational by early July of 1992. Technical problems resulted in significant downtime at St. John and thus few daily samples were collected. At the other sites a majority of the days were successfully monitored. Overall, the summer of 1992 was uncharacteristically "clean". There were few periods when the meteorological conditions were favorable for the build-up of air pollutants. However, there was a measurable amount of variability in the concentrations over time and space and a number of episodes were observed.

The day to day variation in SO<sub>4</sub><sup>2-</sup> and H<sup>+</sup> concentrations at Windsor is shown in Figure 2. Typical for the summer of 1992, the levels of both species tended to be low. There is a clear visual correlation between SO<sub>4</sub><sup>2-</sup> and H<sup>+</sup> with H<sup>+</sup> concentrations (in nmole m<sup>-3</sup>) systematically lower than for SO<sub>4</sub><sup>2-</sup>. Good correlation was observed at all sites, but there was a noticeable increase in the ratio of H<sup>+</sup> to SO<sub>4</sub><sup>2-</sup> at the sites on the east coast (Maritimes). In Figure 3 the mean distribution (in percent) of the main ions is shown. In Ontario, H<sup>+</sup> accounted for a relatively small amount of the cations and NH<sub>4</sub><sup>+</sup> a much large fraction. In contrast, in the Maritimes there was an increase in the amount of H<sup>+</sup> relative to the other ions. This pattern is consistent with the hypothesis that there is less local NH<sub>3</sub> in the Maritime region and potentially less NH<sub>3</sub> during transport if winds are across the ocean.



**Figure 2** The day to day variation in 24 hour sulfate and acidity concentrations measured at Windsor, Ontario, during the spring and summer of 1992.



**Figure 3** The site to site variation in the mean distribution of the major ions found on the fine aerosols collected in eastern Canada.

The changing nature of the aerosol ionic balance can be seen by examining the changes in  $\text{SO}_4^{2-}$  and  $\text{H}^+$  concentration as the episode of Aug. 23-26 is tracked eastward. During this period a large, slow moving high pressure system moved across the northeast North America. As the southerly winds associated with this system's "back side", advected the pollutants northward, varying amounts of  $\text{SO}_4^{2-}$  and  $\text{H}^+$  were observed at the sites depending upon origin of the pollutants and the transport path. In Table 2 the concentrations of  $\text{SO}_4^{2-}$ ,  $\text{H}^+$  and their ratio as a function of site and day are listed. The nature of the aerosol changed dramatically as the episode formed further east. Concentrations increased in southwestern Ontario on the 23<sup>rd</sup> and over Nova Scotia on the 25<sup>th</sup> of August. While  $\text{SO}_4^{2-}$  levels tended to be less in the east there was no such pattern in  $\text{H}^+$ . With the exception of Windsor on the 23<sup>rd</sup>, the highest acidity was observed at Kejimikujik. This was due to less neutralization. The molar ratios of  $\text{H}^+$

to  $\text{SO}_4^{2-}$  were systematically higher at Kejimikujik attaining a value of about 1. This pattern is typical of the measurements over the summer of 1992 and is reflected in Figure 3. In the east the molar ratios were close to 1, while in Ontario and Quebec they were significantly less than 1.

**Table 2** Fine aerosol sulfate concentrations, acidity concentrations and their molar ratios as a function of location and date during the episode observed on August 23-26, 1992.

AUGUST EPISODE [ $\text{H}^+$ ] (nmole $\text{m}^{-3}$ )						
SITE	22	23	24	25	26	27
Windsor	1	<b>283</b>	23	29	5	5
Egbert	6	<b>52</b>	<b>46</b>	32	19	0
Toronto	13	19	<b>39</b>	25	8	0
Montreal	8	19	<b>106</b>	<b>55</b>	59	0
Sutton	13	7	<b>63</b>	<b>104</b>	47	0
Keji	1	9	<b>42</b>	<b>194</b>	<b>183</b>	1

AUGUST EPISODE [ $\text{SO}_4^{2-}$ ] (nmole $\text{m}^{-3}$ )						
SITE	22	23	24	25	26	27
Windsor	14	<b>353</b>	<b>157</b>	<b>137</b>	37	30
Egbert	91	<b>312</b>	<b>257</b>	<b>224</b>	61	7
Toronto	91	<b>195</b>	<b>312</b>	<b>245</b>	59	12
Montreal	86	89	<b>262</b>	<b>219</b>	<b>217</b>	25
Sutton	46	12	<b>152</b>	<b>193</b>	<b>201</b>	6
Keji	8	9	60	<b>204</b>	<b>178</b>	6

AUGUST EPISODE [ $\text{H}^+$ ]:[ $\text{SO}_4^{2-}$ ]						
SITE	22	23	24	25	26	27
Windsor	0.05	<b>0.80</b>	0.15	0.21	0.13	0.17
Egbert	0.07	0.17	0.18	0.14	0.31	0.00
Toronto	0.15	0.10	0.13	0.10	0.16	0.00
Montreal	0.10	0.21	0.40	0.25	0.27	0.00
Sutton	0.29	0.58	0.41	0.54	0.23	0.00
Keji	0.22	<b>1.00</b>	<b>0.70</b>	<b>0.95</b>	<b>1.03</b>	0.13

## SUMMARY

Fine aerosol samples were collected at 7 sites in eastern Canada during the summer of 1992 and sampling is continuing in 1993. There appears to be a clear tendency for less aerosol neutralization over the far eastern regions. Thus, even though  $\text{SO}_4^{2-}$  concentrations are less, the  $\text{H}^+$  concentrations can be the same or even greater than those observed in southern Ontario and Quebec.

Measurement activities are expected to continue through the summer of 1993 with the addition of some sampling in the Vancouver area. Given the relatively large fraction of acid in the aerosols collected over the Maritimes, additional measurements in this area are being considered. In particular, it is necessary to collect information on the aerosol acidity in areas closer to the large population centre of Halifax, Nova Scotia. Over southern Ontario there is a large amount of  $\text{NH}_3$  and the aerosols tend to be relatively neutral. In this region it will be necessary to consider focusing on daytime aerosol acidity measurements. It is possible that much of the neutralization occurs at night when the boundary layer stabilizes. During the day, when people are more likely to be exposed, the acidities could be higher.

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## DEVELOPMENT OF A LOW CUTPOINT VIRTUAL IMPACTOR FOR COLLECTION OF SEMI-VOLATILE ORGANIC COMPOUNDS.

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### ABSTRACT

Traditionally, separation of gas and particulate-phase organics required the use of a diffusion denuder to collect gases placed upstream of the filter pack. We propose a new sampling scheme that includes the following components:

- (i) a virtual impactor (size cut-off of 2.5  $\mu\text{m}$ ) to remove coarse particles from the air sample;
- (ii) a slit-nozzle virtual impactor (size cut-off of 0.15  $\mu\text{m}$ ) to separate the fine particles from the air sample;
- (iii) a particle trap that collects all particles between 0.15 - 2.5  $\mu\text{m}$ ; and
- (iv) a gas trap that collects all gas phase organics (plus a small amount of particulate mass  $d_p \leq 0.15 \mu\text{m}$ ).

A virtual impactor with a 50% cut-off size in the range of 0.1  $\mu\text{m}$  has been developed. The impactor consists of an acceleration nozzle with 0.035 cm in diameter and a collection probe 0.05 cm in diameter. In addition, it operates with a low pressure drop (about 40 inches of water) and with very low particle losses, averaging to about 7% with a maximum of 14 % at the 50 % cut-off size. The separation characteristics of the virtual impactor have been evaluated.

### INTRODUCTION

Inertial impactors have been widely used for particle collection, mainly because of their sharp cut-off characteristics. Due to the extensive theoretical work (Marple and Liu, 1974; Marple and Willeke, 1976) their performance has become well understood and their characteristics can be predicted. The most important limitations of these instruments are the following (Biswas et al, 1988): i) particles may bounce from the collection surface upon impaction. ii) collected particles may reentrain iii) wall losses between the impactor stages may be considerable (Loo et. al, 1976) iv) very large particles may break-up upon impaction, especially at high impaction velocities. The virtual impactor provides an alternative solution to the particle bounce and eliminates reentrainment problems. In order to remove the larger particles from the collection probe, a fraction of the total flow is allowed to pass through the probe, referred to as the minor flow (typically 10% of the total flow). As a result, the concentration of the larger particles in the minor flow has increased by a factor of  $Q_{\text{tot}}/Q_{\text{min}}$  where  $Q_{\text{tot}}$  is the total flow entering the virtual impactor and  $Q_{\text{min}}$  is the minor flow. In addition to the elimination of the particle bounce problem, the virtual impactors have the advantage of keeping the collected particles airborne and, as stated previously, by adjusting the ratio of the minor to the total flow, the concentration of the coarse particles can be increased to a desired value (Barr, et. al, 1983). This paper presents the development of a small cut-off size virtual impactor that operates at a small pressure drop. In addition, a detailed measurement of the particle losses through the system is presented. A better understanding of the particle losses can enable us to optimize the design of small cutpoint virtual impactors.

### METHODS

#### Description of the virtual impactor.

To the best of our knowledge the construction of a 0.1  $\mu\text{m}$  cut-off point virtual impactor has not been accomplished before. The virtual impactor consisted of three parts made of 6061 TG Al. The first

part is the upper plate that includes the acceleration nozzle, where the aerosol enters and gains sufficient momentum for impaction. Two different upper plates were constructed with nozzle diameters equal to 0.025 and 0.035 cm. The second part consisted of the collection tube whose diameter was chosen equal to 0.05 cm so that the ratio of the receiving to the acceleration nozzle was equal to 2 and 1.5, respectively. The distance between the two nozzles was kept constant and equal to 0.020 cm. Finally, the third part was designed as a snap-fit to the second part and consisted of the outlet tube, where the major flow was finally driven through. The three parts were held together by screws. Leaks were avoided by placing O-rings in the contact areas of all three parts.

#### **Experimental.**

The test system for the characterization of the virtual impactor is depicted in Figure 1. Suspensions of 2.5% by weight yellow-green latex microspheres (Fluoresbrite, Polysciences, Warrington, PA) were nebulized by a pocket nebulizer (Retec X-70/N) using room air at 25 psi as described by Zeltner et. al (1991). The nebulizer was connected to a syringe pump in order to atomize large amounts (60 ml) of the fluorescent suspension. In addition, the output of the nebulizer was maintained constant to ensure a stable atomization process. Seven different particle sizes were used: 0.05, 0.12, 0.20, 0.45, 0.75, 1.1 and 2.0  $\mu\text{m}$  in diameter. The particle size range was selected to cover the collection efficiency curve of the virtual impactor, which was designed to have a 50% cut-off size of approximately 0.15  $\mu\text{m}$ . The aerosol was subsequently dried in a 6-liter dry-air dilution chamber by mixing with filtered dry air at a flow rate of 10 LPM and passed through a 1-liter chamber where ten Polonium 210 ionizing units were placed (Staticmaster, NRD Inc.) to neutralize any particle charge. After the neutralizer part of the aerosol was passed through the test system (Figure 1) which consisted of the virtual impactor and two 47 mm glass fiber filters connected to the major and minor flows to collect the test particles. Each filter was connected to a pump with a Matheson mass flow meters in line to control the flows. The aerosol passed through the test system at a total flow rate varying from 0.30 to 0.65 LPM, depending on the acceleration nozzle used. The ratio of minor to total flow varied from 0.1 to 0.2. Another part of the test aerosol was driven through an optical particle size analyzer (model LAS-X Particle Measuring System, Inc., Boulder, CO) which was used to record the particle size distribution throughout the experiment at a sampling flow rate of 1.5 LPM. Finally, the pressure drop across the virtual impactor was continuously monitored in every experiment with a Magnehelic pressure gage (range 0-100 inches of water). In all the experiments the pressure gage showed a pressure drop varying from 35 to 50 inches of water across the virtual impactor, depending on the configuration that was tested.

After a sufficient amount of the aqueous fluorescent suspension was nebulized the two glass fiber filters were extracted using 5 ml of ethyl acetate for each of them, as recommended by the PSL particles manufacturer (Polysciences Inc.). The quantities of the fluorescent dye in the extraction solutions were measured by a fluorometer (FD-300 Fluorescence Detector, GTI, Concord, MA) to determine particle concentration. The efficiency of the virtual impactor was determined by dividing the amount collected on the minor flow filter to the sum of the amounts collected on both major and minor flow filters. Furthermore, the acceleration nozzle, the collection probe and the inside surfaces of the virtual impactor were carefully washed with 10 ml of ethyl acetate each to determine particle losses through the system.

#### **RESULTS AND DISCUSSION**

To initiate the parametric study of the virtual impactor characteristics, a main configuration was chosen. Subsequently, the minor flow ratio, the pressure drop across the virtual impactor and the collection probe to acceleration nozzle ratio were varied, one at a time. Subsequently, the minor flow ratio, the pressure drop across the virtual impactor and the collection probe to acceleration nozzle ratio were varied, one at a time. The main configuration consisted of a jet nozzle diameter equal to 0.035 cm, a collection probe equal to 0.05 cm (therefore the nozzle ratio was 1.5), a total flow through the nozzle equal to 0.56 LPM and a minor flow ratio equal to 0.2. The corresponding pressure drop across the impactor was 35 inches of water. Table 1 shows the results of the virtual impactor characterization. The 50% cutpoint is between 0.1-0.15  $\mu\text{m}$ . As it has been expected, the cutpoint is smaller than the theoretical prediction for an inertial impactor (0.25  $\mu\text{m}$ ). This can be explained by the fact that the minor flow contains 20% of all the particles smaller than the cutpoint. Particle losses reach a maximum around 0.20  $\mu\text{m}$ . The losses in the collection probe increase with the particle size since large particles cross the streamlines and enter the collection probe. Particles smaller than 0.25  $\mu\text{m}$  in diameter are primarily lost on the backside of the acceleration nozzle, as they follow the deflected streamlines of the major flow.

Particles larger than 1.1  $\mu\text{m}$  in diameter are lost inside the acceleration nozzle due to the turbulence that is caused as the flow converges and is rapidly accelerated. This conclusion could be further sustained by examining the deposition pattern of the fluorescent particles in the nozzle using a magnifying lens.

#### **Effect of collection probe to acceleration nozzle ratio.**

In order to test the effect of the collection probe to acceleration nozzle ratio, the smaller of the two acceleration nozzles (0.025 cm diameter) was used to give a ratio of 2. The total flow through the nozzle was 0.29 LPM in order to maintain the same velocity in the acceleration nozzle. The minor flow ratio was 0.2, as in the main configuration. The results of the virtual impactor evaluation is shown in Figures 2. It can be seen that the collection efficiency of the virtual impactor with the increased collection-to-acceleration nozzle ratio drops significantly at smaller particles ( $d_p < 0.25 \mu\text{m}$ ). The most striking result of the increase in the collection probe to acceleration nozzle ratio appears to be the dramatic increase of the particle losses (Figure 3). This result is in agreement with the conclusions of Loo et. al, (1988).

#### **Effect of minor flow ratio.**

The effect of reducing the ratio of the minor flow to the total flow from 0.2 to 0.1 on the virtual impactor characteristics was investigated. The ratio of the collection probe diameter to the acceleration nozzle diameter was 1.5 and the total pressure drop was 35 inches of water at a total flow rate of 0.56 LPM. The results of this test are shown in Table 2. While there seems to be little effect on the collection efficiency, the decrease in the ratio of minor to total flow causes a small increase in the overall particle losses, particularly for particle sizes near the cutpoint. This would be due to the fact that a higher minor flow results in a higher local velocity around the tip of the collection nozzle, and consequently a stronger vacuum is applied to the particles as they exit the acceleration nozzle and approach the proximity of the collection probe.

#### **Effect of increasing the pressure drop across the impactor's nozzle.**

The effect of increasing the jet velocity and therefore the pressure drop across the virtual impactor was investigated. The ratio of the minor to total flow was kept 0.2, the collection probe to acceleration nozzle ratio was equal to 1.5 (the jet diameter was 0.35 mm) and the total sampling flow rate was 0.7 LPM, resulting to a total pressure drop across the virtual impactor equal to 50 inches of water (or, equivalently, 0.12 atmospheres). Figure 4 depicts the efficiency curves for the two pressure drops tested. The collection efficiency increases and the cutpoint decreases as the pressure drop across the virtual impactor increases. This is a direct result of the increase in the jet velocity and the subsequent decrease in the impactor's cutpoint. The particle losses decrease as the jet velocity increases (Figure 5). In the case of the increased jet velocity, the particle losses become maximum for particles equal to 0.12  $\mu\text{m}$  in diameter, as opposed to the main configuration, where the loss maximum occurred for particles of 0.20  $\mu\text{m}$  in diameter.

#### **CONCLUSIONS.**

A virtual impactor with a 50% cut-off size in the range of 0.1  $\mu\text{m}$  has been developed. The impactor consists of an acceleration nozzle with 0.035 cm in diameter and a collection probe 0.05 cm in diameter. In addition, it operates with a low pressure drop (about 40 inches of water) and with very low particle losses, averaging to about 7% with a maximum of 14 % at the 50 % cut-off size. The results can be summarized as follows:

- (1) The 50% cut-off size decreases as the collection probe to acceleration nozzle ratio increases from 1.5 to 2. In addition, the particle losses through the impactor increase.
- (2) The collection efficiency of the virtual impactor is not significantly affected by a decrease of the minor flow ratio from 0.2 to 0.1. This decrease in the flow ratio, however, is followed by an increase in the particle losses, particularly for sizes near the impactor's 50% cutpoint.
- (3) Increasing the jet velocity and therefore the pressure drop across the impactor's nozzle results in a decrease in the 50% cut-off size, as well as in a decrease in the particle losses across the virtual impactor.

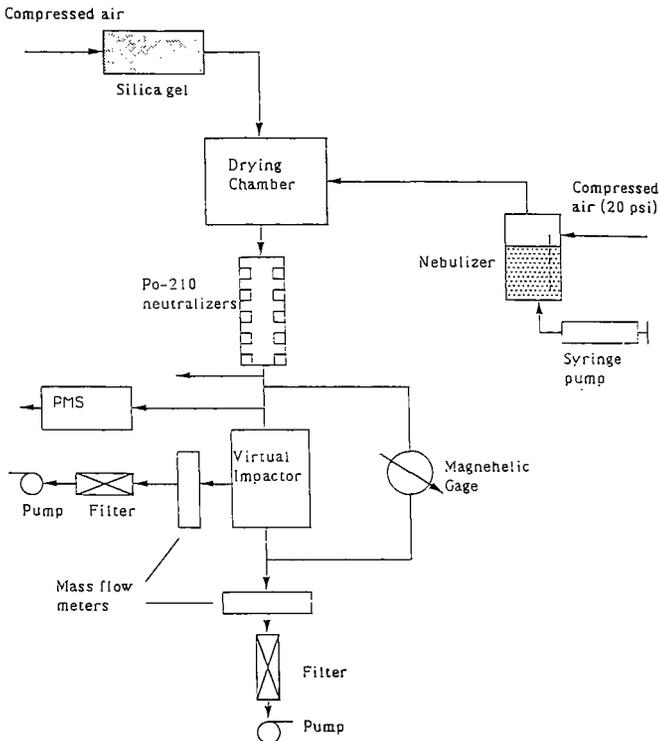
#### **ACKNOWLEDGEMENTS.**

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816740. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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**FIGURE 1.** Schematic diagram of the test system.

**Table 1. Particle collection characteristics of the virtual impactor.**

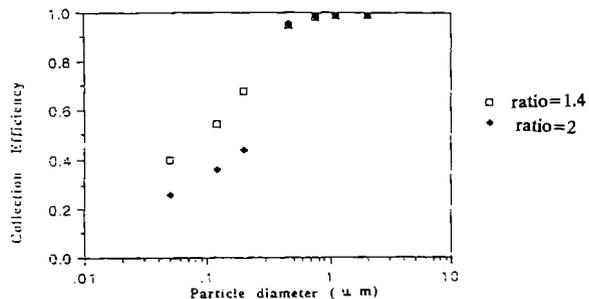
Particle Diameter ( $\mu\text{m}$ )	(%) in Major Flow (0.44 LPM)	(%) in Minor Flow (0.12 LPM)	(%) Collection Efficiency	(%) Total Losses	(%) Losses on inlet of nozzle	(%) Losses on collection probe	(%) Other interstage losses
0.05	45.1	38.2	45.9	10.4	2.2	3.4	1.8
0.12	41.4	50.5	55.0	8.1	1.0	3.8	3.3
0.20	33.5	52.6	61.1	13.8	3.8	5.5	4.5
0.45	4.8	89.3	94.9	5.9	1.3	3.1	1.5
0.75	1.9	95.5	98.0	2.6	0.2	1.9	0.5
1.10	1.8	93.6	97.1	4.6	1.1	2.1	1.4
2.00	1.6	91.4	98.3	7.0	3.4	2.8	0.8

- a. The values in the table represent averages of repeated runs.  
 b. The minor flow ratio was 0.2.  
 c. The collection probe to acceleration nozzle ratio was 1.4 (nozzle diameter 0.035 cm)

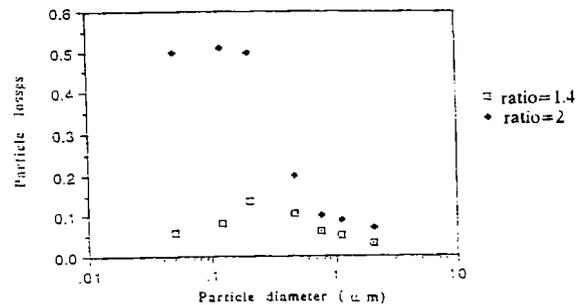
**Table 2. Particle collection characteristics of the virtual impactor with a minor flow ratio 0.1.**

Particle Diameter ( $\mu\text{m}$ )	(%) Collection efficiency	(%) in Major Flow (0.5 LPM)	(%) in Minor Flow (0.06 LPM)	(%) Total losses	(%) Losses on inlet of nozzle	(%) Losses on collection probe	(%) Other interstage losses
0.05	39.9	55.0	36.5	8.4	0.9	2.6	4.9
0.12	50.2	38.8	39.1	22.1	5.5	10.2	6.4
0.20	58.3	34.0	47.5	18.8	6.4	10.9	1.5
0.45	94.5	5.1	87.8	9.0	3.1	4.2	1.7
0.75	99.7	0.3	94.5	5.2	3.2	1.4	0.6
1.10	99.8	0.2	98.1	1.2	1.2	0.0	0.0
2.00	100.0	0.0	98.9	1.1	0.7	0.4	0.0

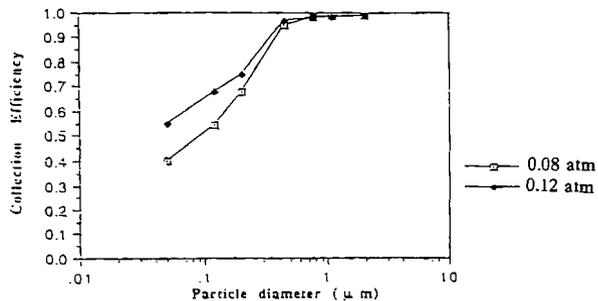
- a. The values in the table represent averages of repeated runs.  
 b. Collection probe to acceleration nozzle ratio 1.4.  
 c. Acceleration nozzle diameter 0.035 cm.



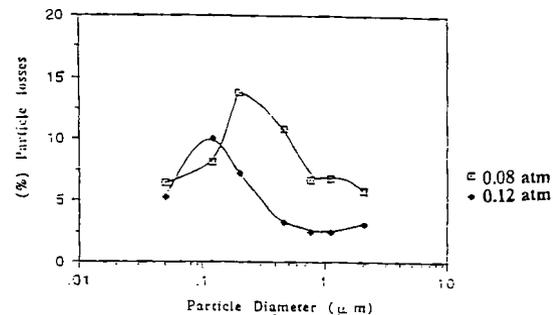
**FIGURE 2.** Collection efficiency for different collection probe to acceleration nozzle ratios.



**FIGURE 3.** Particle losses for different collection probe to acceleration nozzle ratios.



**FIGURE 4.** Collection efficiency for different pressure drops across the virtual impactor.



**FIGURE 5.** Particle losses for different pressure drops across the virtual impactor.

***Session 22***

***Personal Monitors***

## Evaluation of a Portable Multisorbent Tube Sampler for Monitoring Airborne Organic Compounds

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### ABSTRACT

The Perkin Elmer STS 25 Sequential Tube Sampler is a novel portable sampling device for characterizing volatile organic compounds (VOCs) in air. The STS 25 is a self-contained unit that is designed to collect air samples consecutively onto a batch of up to 24 sorbent tubes, one at a time, at a specified flow rate for a preselected collection time per tube. The device was evaluated under stringent laboratory conditions using a standard mixture containing 42 nonpolar VOCs and packing the tubes with a three-stage carbon-based multisorbent bed. Samples were analyzed noncryogenically using a Perkin Elmer ATD 400 Auto Thermal Desorption system and gas chromatograph.

Results of these analyses indicated that the target compounds were collected with efficiencies generally comparable with those obtained with the standard (TO-14) procedure for canister sampling followed by cryogenic preconcentration and GC analysis. An outdoor sample collected with the device also yielded results that compared favorably with those obtained using the TO-14 methodology. The portability and ease of operation of the STS 25 lend itself to use in various microenvironments to provide both temporal and spatial information on VOCs in complex indoor and outdoor atmospheres.

### INTRODUCTION

Recognition of the importance of trace-level VOCs in breathing-zone air and their potential impact on human health has stimulated interest in methods for characterizing these compounds. Most of the techniques in use today for measuring VOC concentrations have their origin in industrial hygiene monitoring methods. They generally rely on solid sorbents<sup>1,2</sup> or containers<sup>3</sup> to collect whole-air samples.

A recent development in efforts to measure temporal variability of VOCs is the Perkin Elmer Sequential Tube Sampler (STS 25), which is designed for use with their Automated Thermal Desorption system (ATD 400) and gas chromatograph (GC). The present study was undertaken to evaluate the performance of the Perkin Elmer STS 25. Before the evaluations were begun, a method for analyzing TO-14 compounds using a three-stage carbon-based multisorbent bed for sample collection, along with the ATD 400's electrically cooled two-stage carbon-based trap for refocusing the desorbed sample, was developed and validated.

### EXPERIMENTAL

#### Sequential Tube Sampler (STS 25)

The STS 25 air sampler is a prototype unit supplied by Perkin Elmer (Figure 1). The device consists of an air-tight plastic box that contains a sample tube carousel, an electronic timer, and a personal monitoring pump. A fan mounted in the rear of the unit draws air into the box at a rate of ~30 L/min, which is sufficient to change the air above the sample tubes once every second. The air enters through an opening in the lid which is positioned above the collection tubes. The air stream is sampled by the one collection tube that is located in the single position that allows the air monitoring pump to draw the air through a tube. When not in the sampling position, the tubes are effectively sealed from the air stream through the use of diffusion-limiting caps.

The sample volume is regulated by time and flow rate. The timing device in the STS 25 will maintain a tube in the sampling position from 0.1 sec to 10 hr. During this study, each tube was sampled for 75 min.

At the end of the sampling period, the carousel rotates and the next tube is positioned to receive an air sample. An SKC Model 224-PCXR7 personal monitoring pump was used to draw air through the tube and was operated at a nominal flow rate of ~43 cc/min. This flow setting resulted in a 40 cc/min flow through the packed sampling tube. All flow rates were confirmed using a Buck Model M-5 calibrator.

Power for the STS 25 can be obtained either from a rechargeable 12 v battery or from a DC power supply/battery charger. The DC power unit was used throughout this study. The STS 25 is also capable of maintaining a trickle charge to the battery of the personal monitoring pump, which ensures that the performance of the pump remains constant over long sampling periods.

During the evaluation of the STS 25, carbon-based sorbents were used to collect the target VOCs. The three-staged tubes (based upon Supelco, Inc.'s Carbotrap 300 configuration) contained Carbotrap C (300 mg), Carbotrap (200 mg), and Carbosieve S-III (125 mg). These were maximum mass loadings for the sampler tubes yet still allowed all of the sorbents to be positioned in the heated zone of the tube during desorption.

#### Sorbent Tube Analysis

Sorbent tubes used during the evaluation of the STS 25 were processed using the ATD 400/GC system. Typical operating conditions for the thermal desorption of a tube included desorption of the sample at 325 C for 10 min with a purge flow of 60 cc/min helium carrier. The refocusing trap was packed with 35 mg of Carbotrap and 23 mg of Carbosieve S-III. While receiving the organic components from the heated sampler tube, the trap was held at 4 C, then was thermally desorbed at 325 C for 3 min. A trap desorption flow rate of ~11 cc/min was maintained to accomplish a rapid transfer of the refocused sample material to the GC.

The gas chromatograph was operated with a 50 m x 0.32 mm x 5.0  $\mu$ m dimethyl polysiloxane fused silica capillary column in conjunction with a flame ionization detector. Analytical conditions for the resolution of the TO-14-based target compounds included an initial oven temperature of 40 C for 15 minutes, then the oven was heated at 8 C/min to a final temperature of 200 C and held at this temperature for 12 min. A standard TO-14 cryogenic analytical system was also used during this study as a reference system to compare results obtained using the carbon-based sorbent traps.

#### STS 25 Evaluation Experiments

The STS 25 was subjected to three types of tests. Firstly, it was mechanically tested to determine if it would reliably cycle as specified to collect air samples using sorbent tubes. Secondly, the STS 25 was placed in a 75-L glass/stainless steel environmental test chamber and programmed to collect blank (zero air) air samples and samples of TO-14 standard atmospheres at 2 and 10 ppbv concentrations. The unit was challenged at two temperature levels (25 C and 37 C) and two relative humidity (RH) levels (10 percent and 60 percent). In all cases, 3-L samples were collected. The tubes were analyzed and the results were compared to those from an initial chamber validation test to determine whether the STS 25 unit was able to collect laboratory-controlled atmospheres without either contributing to, or removing, any of the TO-14 target compounds. Finally, a field test was performed to evaluate the STS 25 unit under "real world" conditions. The STS 25 was set up to collect a 3-L outdoor ambient air sample. Simultaneously, a second sorbent tube and a 6-L air sampling canister were used to sample the air at the same location. A Tylan-controlled pumping assembly drew air through this second tube at the same 40 cc/min flow rate as the STS 25 was using. The pre-evacuated canister was filled using a restrictive orifice that allowed air to enter the canister at ~60 cc/min. This flow decreased to ~40 cc/min as atmospheric pressure was approached during the 75-min collection period. At the end of the sampling period, the canister was still at subatmospheric pressure (~200 mm Hg). Data from these collection systems were compared to evaluate both the operation of the STS 25 system and the performance of the sorbents used.

## RESULTS AND DISCUSSION

### Mechanical

The STS 25 was operated over two 24-hr periods to evaluate the operational characteristics of the unit. The device was programmed to collect 75-min and 10-min samples. In both cases, the system performed with no mechanical problems. The charging system on the STS 25 also performed well. The SKC personal monitoring pump maintained a constant flow rate (~43 cc/min) over a 24-hr period. No mechanical problems were encountered with the operational aspects of the STS 25.

### Environmental Chamber Tests

**Blank Test.** The results for the background samples collected by the STS 25 are shown in Table 1A. With the STS 25 present in the chamber several of the TO-14 target compounds were observed. The 25 C runs indicate that the concentrations of these compounds change slightly with RH. The 37 C run shows higher concentrations, which are probably due to compounds being liberated from the STS 25 itself. It is important to note that the conditions under which all the chamber tests were run reflect a very stringent test of the artifact characteristics of the STS 25. Since the device is in a relatively small volume that is being purged at 2 L/min, while the STS 25 is cycling air through itself at 30 L/min, it is evident that any volatile compounds that may be associated with the materials used in the construction of this sampler are being concentrated in the chamber atmosphere. Nonetheless, the blank test does indicate that there is the potential for artifact contribution from the STS 25 during ambient air sampling.

Canister samples were also collected from the chamber while the STS 25 was drawing the sample onto the collection tube. Differences were identified between the tube concentrations and the canister analysis. We believe that these discrepancies are indications of the limitations associated with quantifying complex mixtures with only an FID detector. The differences observed were generally in a direction that indicated compounds at higher levels with the STS 25 tubes than with the canister samples. This is not surprising because compounds other than the TO-14 species could be eluting at the same time as one of the target compounds and are not distinguished on the basis of retention times only.

**TO-14 Chamber Tests.** The STS 25 results (Table 1B and 1C) tend to exaggerate the concentrations present for several of the earliest eluting species. We believe that this is a further example of artifact compounds coeluting with compounds of interest. This exaggeration is particularly evident in the 2 ppbv test where a slight contribution from an artifact results in a pronounced variance in recovery. Relative humidity does not seem to play as much of a role in liberating light artifacts as does the increased temperature. The reported concentration values from the STS 25 were confirmed to be due to artifact coelution since the canister results generally did not reflect increased TO-14 species presence with changes in relative humidity and temperature.

The canister results for early eluting TO-14 species were generally at expected levels. A noticeable deviation was that methyl chloride (not shown in the table) was consistently reported with low recoveries. This could be indicative of compound affinity for the STS 25 sampler.

The intermediate eluting compounds in the TO-14 mixture exhibited predictable recoveries. At 10 percent RH, STS 25 recovery data were generally lower than at the 60 percent RH level at 25 C. This is in agreement with the results observed earlier where the presence of humidity seems to enhance the desorption of these TO-14 species from the multisorbent collection bed. Also, agreement with the canister results was generally more reproducible. It appears that this region of the chromatogram was affected less by artifact contributions from the STS 25. Therefore, FID quantitation was more reliable and this was reflected in the reported concentrations for both the 25 C and 37 C tests.

The final set of compounds in the TO-14 mixture were the latest eluting species. From the STS 25 blank test run it was observed that there was a group of artifact peaks that eluted at the same time as these heavy TO-14 species. Because of this, artifact coelution, with contribution to the reported STS 25 values, was

expected and observed. For the 2 ppbv test, higher concentrations were reported when compared to the canister results. This was particularly true for the 37 C test. However, canister levels were also elevated in this region, indicating that the STS 25 at 37 C was liberating TO-14 species along with nontarget compounds. One particular compound, 1,2,4-trimethylbenzene, was identified by both the tube and canister results as being a major TO-14 artifact associated with the sampler.

The general statement that can be made from evaluating the STS 25 under stringent laboratory conditions is that the sampler will collect TO-14 compounds onto sorbent tubes. The Perkin Elmer sampler apparently does contribute artifacts to the sampling process when operated in a confined environment that does not afford an air changeover rate that is as great as that of the STS 25 itself. Also, the analytical system employed was limited by the use of only the FID detector, which was affected by coeluting artifacts. Nonetheless, the STS 25 operated acceptably within the confines of the testing environment, sorbents, and analytical system used.

Outdoor Sampling. The outdoor air sampling results, for selected compounds, from the analysis of the two sorbent tubes using the ATD 400/GC and the canister using the GC/MSD system are presented in Table 1D.

Agreement between the two tube samples was quite good with the same compounds being identified and comparable concentrations reported. From this information it was evident that when used in a less confined environment, the STS 25 collects a representative air sample.

The canister samples however did not quantitatively reproduce the tube data. This was particularly true for the early eluting peaks. Variability is again judged to be associated with the qualitative/quantitative differences of the FID and MSD detectors and is not necessarily indicative of deficiencies with the STS 25 as a sampling unit or the sorbents used. In general, analytical agreement for this sampling was quite good and may be attributed to the less complex nature of the sample allowing better FID identification and quantification.

A copy of the FID traces from the two collection tubes is provided in Figure 2. It should be noted that the relative humidity during the collection of these samples was at ~90 percent. It can be seen on both of the FID traces that there was a negative deflection in the baseline prior to the elution of the VOCs. Although the flame did remain lit, the conditions may have been close to the tolerable moisture limit for the FID.

## CONCLUSIONS

The STS 25 is a portable, easy to use, sampling device which provides an important option for monitoring ambient air toxic compounds with carbon-based sorbent sampling tubes. The evaluation of the unit indicates that it is mechanically sound and able to collect TO-14 VOCs with comparable efficiency to canister sampling. Limitations of the system are that if it is operated in very confined environments, it is possible that the sampler may contribute to or alter actual VOC levels. However, when used as intended, sample integrity is not compromised by the unit. To be able to correctly analyze the sorbent tubes collected by the STS 25, it is recommended that GC analysis be combined with mass selective detection, compound specific detectors, or dual FIDs with two-dimensional chromatography.

## ACKNOWLEDGEMENTS

The authors wish to express thanks to Perkin Elmer, both in the United Kingdom and U.S.A., for assistance during this study. The information presented here has been funded wholly or in part by the U.S. Environmental Protection Agency under Contract Number 68-D0-0007 to Battelle Memorial Institute. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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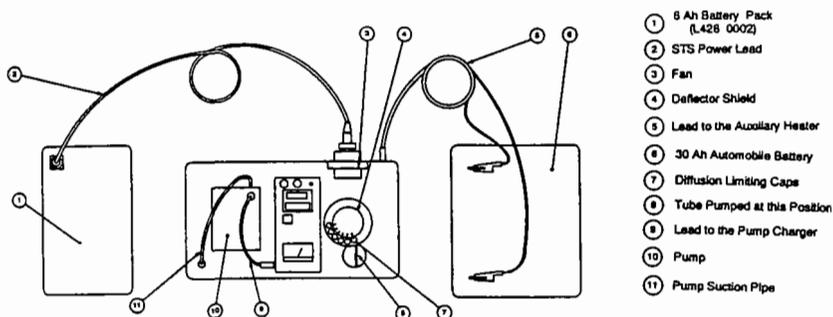


Figure 1. STS 25 schematic.

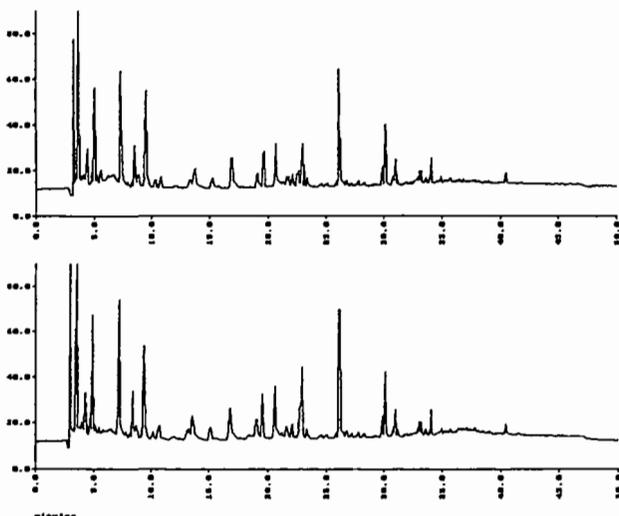


Figure 2. FID traces of outdoor air sampling: STS 25 upper, Tylan tube lower.

Table 1. Results for selected compounds during the STS 25 evaluation.

Sampler and Atmosphere	Temp (°C)	Relative Humidity (%)	Compound Concentration (ppbv)			
			1,3-Butadiene	Benzene	Toluene	m/p-xylene
<b>A. Blank</b>						
STS 25	25	10	0.1	0.4	0.5	0.7
Canister	25	10	n.d.*	0.1	0.2	0.4
STS 25	25	60	0.4	1.3	0.6	1.0
Canister	25	60	n.d.	0.1	0.1	0.5
STS 25	37	60	0.9	2.8	2.1	1.9
Canister	37	60	n.d.	0.2	0.7	1.5
<b>B. 2 ppbv, TO-14</b>						
STS 25	25	10	2.3	1.9	1.6	1.8
Canister	25	10	1.3	2.1	1.6	1.6
STS 25	25	60	3.3	3.6	2.3	2.1
Canister	25	60	1.8	2.0	1.9	1.5
STS 25	37	60	4.7	3.4	2.5	3.1
Canister	37	60	2.0	2.5	1.9	3.1
<b>C. 10 ppbv, TO-14</b>						
STS 25	25	60	11	11	11	9
Canister	25	60	13	12	13	10
STS 25	37	60	9	10	10	8
Canister	37	60	12	12	14	15
<b>D. Outdoor Sampling</b>						
STS 25	21	90	3.2	1.4	3.0	2.2
Tylan tube	21	90	2.7	1.8	3.5	2.2
Canister	21	90	n.d.	1.5	3.4	2.4

\* n.d. = not detected.

***Session 23***

***General***

## Sensitive Real-Time Monitoring of NO, NO<sub>2</sub> and other Nitrocompounds Under Atmospheric Conditions

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**ABSTRACT:** A new laser-based technique has been developed recently for the detection of NO, NO<sub>2</sub> and other nitrocompounds in the vapor phase. Atmospheric sampling is accomplished using a standard pulsed valve/molecular beam apparatus. Supersonic expansion of the sample cools the gas and facilitates spectroscopic detection. A fraction of the expanded gas is transmitted in the form of a molecular beam into the analysis chamber which is differentially pumped. There the molecular beam is probed by a laser beam tuned to the A<sup>2</sup>Σ<sup>+</sup> ← X<sup>2</sup>Π (0,0) transition of NO at 226 nm. Molecules of NO in this region are photoionized by a (1+1) resonance-enhanced multiphoton ionization (REMPI) process and accelerated into a time-of-flight mass spectrometer (TOFMS) for mass selective detection. In addition to NO species, NO<sub>2</sub> and other nitrocompounds are detected efficiently by employing a single laser operating at 226 nm or 193 nm to both photofragment the target molecule and detect the NO fragments, produced as a result of the rapid predissociation of NO<sub>2</sub>. In this manner, total NO<sub>x</sub> can be measured simultaneously using a single excitation wavelength for NO and NO<sub>2</sub> detection. Results of studies of the laser photofragmentation/ionization technique using laser radiation at 226 nm and also at 193 nm are presented and discussed.

**INTRODUCTION:** Atmospheric NO and NO<sub>2</sub> are important participants in several atmospheric reaction cycles, including the role of NO as a precursor in the production of atmospheric HNO<sub>3</sub> (acid rain) and its role in the photochemical production of O<sub>3</sub>. Despite the importance of these species in the atmosphere, they are generally only present at trace levels making quantitative measurements difficult. Concentrations may range from the parts-per-trillion (ppt) to parts-per-million (ppm) in parts of the lower atmosphere. A common method of detection for the NO molecules is the chemiluminescent reaction of NO with an excess of O<sub>3</sub> producing O<sub>2</sub>, and NO<sub>2</sub><sup>\*</sup> which is detected optically. Another method of detection is laser induced fluorescence which has been developed by Bradshaw, Davis, Rodgers and co-workers and demonstrated to be an effective method of detection both for surface and airborne applications.<sup>1,2</sup>

The detection of NO<sub>2</sub> is often accomplished indirectly. Independent measurements of NO and NO<sub>x</sub> are performed, and the NO<sub>2</sub> is determined from the difference of the two measurements. NO<sub>2</sub> can also be detected directly by long path absorption methods.<sup>3</sup> An indirect method for measuring NO<sub>2</sub> is to detect the laser induced fluorescence of NO molecules which are produced from the UV photolysis of NO<sub>2</sub>. This method of photofragmentation-fluorescence using a two-laser pump/probe technique has been used to detect a number of species (see references 4-15) and has been successfully applied by Davis, Rodgers and coworkers to detect atmospheric NO<sub>2</sub>, HONO and other species.<sup>14,15</sup> The analytical sensitivities that can be achieved by this method approach the ppt level and

are superior to other non-laser based methods. Unlike long path absorption techniques, the photofragmentation/fluorescence method provides a point measurement allowing accurate spatial profiling of the atmospheric environment.

We have developed recently a technique for the detection of NO, NO<sub>2</sub> and other nitrocompounds which employs a single laser operating at 226 nm. The laser radiation is used for both photofragmentation of nitrocompounds, which results in the production of NO fragments, and resonance-enhanced multiphoton ionization (REMPI) with time-of-flight (TOF) mass spectrometric detection of NO molecules via the  $A^2\Sigma^+ \leftarrow X^2\Pi$  (0,0) band.<sup>16</sup> The technique has been demonstrated using a pulsed valve/molecular beam time-of-flight apparatus. Supersonic cooling results in greatly simplified spectra of both analyte and potential spectral interferent species thus increasing the selectivity of the approach. We have extended this technique to include the use of 193 nm radiation for photofragmentation and ionization of the NO species. In this paper, we discuss the results of studies performed at both 226 nm and 193 nm.

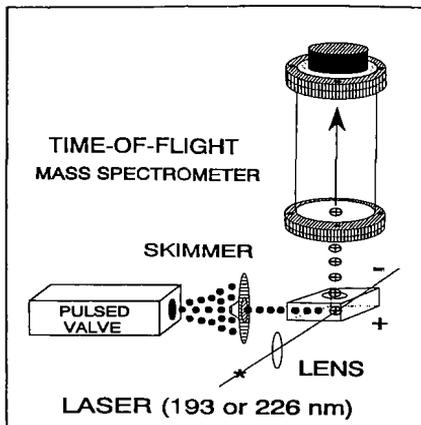


Figure 1: Schematic of the apparatus

**EXPERIMENTAL:** The experimental apparatus has been described previously.<sup>16</sup> A schematic diagram of the salient features of the apparatus is shown in Figure 1. Briefly, sample introduction was performed at atmospheric pressure where the sample was present as a minor species in a buffer gas (usually Ar or air). Calibrated mixtures of NO/Ar (0.1%) and NO<sub>2</sub>/air (6.2 ppm) were obtained from Matheson and Scott-Marrin respectively. Samples of nitromethane (from Aldrich), dimethylnitramine (from ARDEC) and nitrobenzene (from Eastman-Kodak) were introduced in flows of the buffer gas where the concentrations were calculated using the reported vapor pressures at room temperature. The gas mixtures were expanded into the analysis chamber using a pulsed valve (R.M. Jordan Co.) operated at 10 Hz which had a nozzle diameter of 0.5 mm. Following expansion, the sample species were probed by laser radiation at 226 nm or 193 nm which was focused by a lens ( $f=250$  mm or  $f=500$  mm lenses). The laser radiation induced fragmentation of the parent species to produce NO fragments which were subsequently ionized within the same laser pulse by REMPI processes. An excimer pumped dye laser system with frequency doubling (Lumonics Ltd., Hyper EX-400, Hyper DYE-300 and Hyper TRAK-1000) operated at 10 Hz provided tunable UV radiation at 226 nm with maximum pulse energies of approximately 200  $\mu$ J and a spectral linewidth of 0.16  $\text{cm}^{-1}$ . An ArF excimer laser (Lambda Physik Inc. EMG-150) provided broadband UV radiation (approximately 100  $\text{cm}^{-1}$ ) at 193 nm with pulse energies in the chamber of 1-5 mJ. Ion signals from the TOF mass spectrometer were displayed and monitored on a 125 MHz oscilloscope (LeCroy 9400). Signals were also directed to a gated integrator (Stanford Research Systems) whose output was acquired by a PC-AT for data analysis and storage.

The TOF mass spectrometer distinguishes ions of different masses by their different

times of arrival at the microchannel plate detector which is located at the end of the flight tube. Since all the ions produced in the ionization region experience the same potential, they have the same kinetic energy and are separated in time according to their masses. Although the overall time of arrival of a given ion depends on the sum of the transit times through various regions of the TOF mass spectrometer, it is proportional to the square root of the mass of the ion. The time of arrival  $t_1$  of mass  $m_1$  is related to the time of arrival  $t_2$  corresponding to mass  $m_2$  by the following:

$$\frac{t_1}{t_2} = \frac{m_1^2}{m_2^2} \quad (1)$$

Thus the determination of any mass,  $m_2$  can be performed using an accurate measurement of  $t_1$  of a known mass  $m_1$ . In the current studies,  $\text{NO}^+$  was used to calibrate the time-of-flight mass spectral response.

The pulse pressure of the gas in the sample chamber was calculated using the following equation (adapted from reference 15):

$$P_{\text{pulse}} = P \left( \frac{r}{R} \right)^2 (1 - \cos^3 \theta) \quad (2)$$

In the above equation  $P$  is the backing pressure,  $r$  is radius of the nozzle orifice,  $R$  is the radius of the skimmer orifice and  $\theta$  is the skimmer transmission angle, which is equal to the arctangent of  $R$  over  $D$ , the distance of the nozzle to the skimmer. For a backing pressure of 770 Torr, a nozzle diameter of 0.5 mm, a skimmer diameter 3.0 mm and a skimmer to nozzle distance of 20 mm, the pulse pressure in the chamber is approximately 180 mTorr.

**RESULTS AND DISCUSSION:** The physical processes underlying our method for detecting nitrocompounds by using a single laser may be understood by referring to Figure 2 which shows partial energy level diagrams for the  $\text{NO}_2$  and  $\text{NO}$  molecules. By restricting ourselves to using 226 nm radiation, it is found that nitrocompounds, generalized as  $\text{R-NO}_2$ , which are irradiated at this wavelength will photofragment with high efficiency to produce the  $\text{NO}_2$  fragment and the radical  $\text{R}$ . The  $\text{NO}_2$  molecule can then be detected using the same laser by monitoring its predissociative product,  $\text{NO}$ , by (1+1) REMPI using the  $\text{A}^2\Sigma^+ \leftarrow \text{X}^2\Pi$  (0,0) band at 226 nm. Alternatively,  $\text{NO}$  fragment detection can be accomplished by LIF at the same wavelength. However it was determined in this study that the LIF approach is not as effective for the  $\text{NO}/\text{NO}_2$  system.

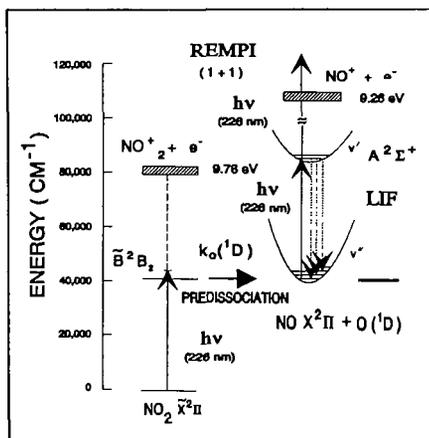


Figure 2: Potential energy level diagram of  $\text{NO}$  and  $\text{NO}_2$

Presented in Figure 3 is a typical mass

spectrum obtained when photolyzing a 130 ppm mixture of dimethylnitramine (DMNA) in Ar using 226 nm radiation. The DMNA molecule was chosen for study because it is a simple analogue for larger nitramine molecules which are of military interest. The spectrum is characteristic of all the compounds studied at this laser wavelength in that it shows a prominent ion signal whose time-of-arrival corresponds to  $m/e=30$  amu which is that of the  $\text{NO}^+$  ion. Similar results were obtained using Ar, air or nitrogen as the buffer gas. No ion signal was recorded, however, when the laser was tuned away from resonance. The striking simplicity of the ion mass spectrum and lack of any other significant signals indicates that the ionization is the result of a fragmentation/REMPI process. It is important to note that ion signals corresponding to the mass of  $\text{NO}_2$  ( $m/e=46$  amu) were not observed in the mass spectra for any of the nitrocompounds studied. This supports the proposed mechanism which relies on rapid predissociation of the  $\text{NO}_2$  to produce NO. To verify the mass spectral assignment and also to maximize the signal intensity, an ion excitation scan was performed. This excitation spectrum reveals numerous rotational lines which are attributed unequivocally to electronic transitions of the  $\text{NO } A^2\Sigma^+ \leftarrow X^2\Pi$  (0,0) band.

In addition to using 226 nm radiation, we have investigated the use of 193 nm radiation for photofragmenting and ionizing nitrocompounds. Ionization of NO molecules is possible by way of the  $A^2\Sigma^+ \leftarrow X^2\Pi$  (3,0) and  $B^2\Pi \leftarrow X^2\Pi$  (7,0) bands and the  $D^2\Sigma^+ \leftarrow X^2\Pi$  (0,1) vibrationally excited band. The fragmentation

of nitrocompounds at 193 nm to produce NO occurs in a way that is similar to the fragmentation processes at 226 nm. While the precise mechanisms are not known, recent studies by Houston and coworkers<sup>9</sup> of the 193 nm photodissociation of nitromethane indicate that the  $\text{NO}_2$  fragment is produced in a number of excited states which are further fragmented to produce NO either in its electronic  $X^2\Pi$  ground state or directly in its excited  $A^2\Sigma^+$  state. It is also expected that the NO fragments have a distribution of energies. The energy distribution makes it possible for several of the rovibrational levels in the  $X^2\Pi$  state to be resonant with the relatively broad spectral output of the ArF excimer used as the fragmentation/ionization source. The relatively higher sensitivity that is obtained for NO photofragments from nitrocompounds (as opposed to pure NO) is a combined result of

the production of electronically excited NO molecules and a distribution of rotationally and vibrationally excited NO molecules in the  $X^2\Pi$  state. By comparison, pure NO molecules that undergo supersonic expansion are restricted to a few rovibrational levels, some of which may not be in resonance with the ArF laser output. Thus it is likely that a relatively smaller fraction of the pure NO population is accessible by the laser for photoionization.

Presented in Table 1 are limits of detection (LODs) for the compounds studied employing the fragmentation/REMPI technique using 226 nm and 193 nm radiation. The LODs range from ppm to ppb and refer to the gas phase concentration of the analyte prior to

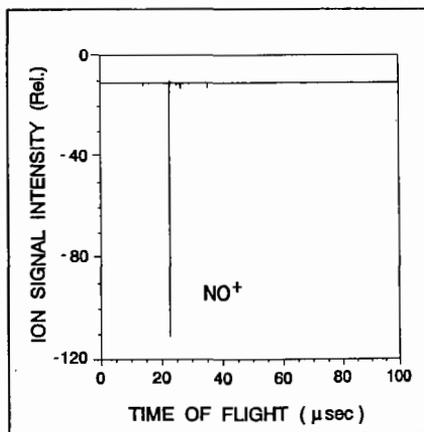


Figure 3: Time-of-flight mass spectrum of DMNA

introduction into the analysis chamber. The experimental conditions for all of these determinations were identical, thus any differences in the LODs are indicative of differences in the absorption cross sections and/or fragmentation efficiencies of the precursor molecule, as well as the absorption cross section NO fragment at the respective wavelengths. For a backing pressure of approximately 1 atm (atmospheric sampling conditions), the calculated gas volume throughput of the supersonic nozzle is  $6.8 \text{ Torr/cm}^3$  in a pulse of about  $100 \mu\text{s}$

duration. In this work, a LOD of 8 ppb for NO (for laser excitation at 226 nm) corresponds to a density of  $5 \times 10^7 / \text{cm}^3$  in the probe volume of the laser. Using a laser induced fluorescence technique, Sandholm et al.<sup>14</sup> have reported a LOD of  $9.4 \times 10^7 / \text{cm}^3$ . For NO<sub>2</sub>, a LOD of 240 ppb corresponds to a density of  $1.4 \times 10^9 / \text{cm}^3$  in the probe region. Sandholm et al.<sup>14</sup> have reported a LOD for NO<sub>2</sub> of  $4 \times 10^8 / \text{cm}^3$  using a related two-laser photofragmentation/two-photon laser induced fluorescence technique. However, this technique requires an integration period of up to 6 min. in order to achieve its maximum sensitivity while our present technique is virtually real-time in its response. Plane and Nien<sup>3</sup> have used a differential absorption spectrometry technique operating in the UV to measure tropospheric NO<sub>2</sub>. They have achieved an LOD of  $1.6 \times 10^{10} / \text{cm}^3$  but require an integration time of 4 min and a pathlength of 5 km. Their technique is also susceptible to absorption interferences and can only provide an average concentration value over the path of observation.

Concentrations of NO and NO<sub>2</sub> in the troposphere may range from the ppt to the low ppm which requires that a method of analysis possess a linear dynamic range over as much as 7 orders of magnitude. At 226 nm, the linear dynamic range (LDR) is about 5 orders of magnitude extends from the LOD to over 100 ppm for NO. At higher concentrations, the microchannel plate detector saturates resulting in a nonlinear response. The LDR at 193 nm is about 3 orders of magnitude for NO and is limited by the LOD which is approximately 1 ppm. Similar LDRs are obtained for the NO<sub>2</sub> molecule at both wavelengths. With modifications to the present system design, it is expected that the sensitivity can be improved upon significantly so that lower LODs and larger LDRs can be achieved at both 226 nm and 193 nm.

Improvements on the current system will include a higher power laser system. It was determined in these studies that the laser energies used were insufficient to saturate the observed ion signals. Higher laser pulse energies will lead to saturation of the ion signals which will enhance the sensitivity and improve the signal-to-noise characteristics of the measurements. Higher pulse energies will also allow the sample volume probed by the laser to be expanded leading to an increase in sensitivity. Another improvement to the current system will be a more efficient sampling apparatus. The pulsed valve used for sample

Table 1: Limits of Detection at 226 nm and 193nm

Compound	LOD at 226 nm (ppb)	LOD at 193 nm (ppb)
NO	8	1200
NO <sub>2</sub>	240	500
CH <sub>3</sub> NO <sub>2</sub>	1000	180
DMNA	450	510
Nitrobenzene	2400	490

introduction in these studies is not designed for trace analytical applications and is estimated to transmit less than 1% of the sample gas pulse to the probe region of the apparatus. The valve could be modified to deliver a much higher fraction of the sample into the apparatus.

**CONCLUSION:** A new technique for the sensitive and selective detection of NO, NO<sub>2</sub> and other nitrocompounds which employs a single laser for both photofragmentation and REMPI of the target molecules has been demonstrated. Similar to previous photofragmentation/fluorescence techniques, the current technique is characterized by real-time response, a large linear dynamic range and high sensitivity. The photofragmentation/REMPI technique, which has been demonstrated at 226 nm and 193 nm using a low energy frequency-doubled tunable dye laser and an ArF excimer laser, respectively, already achieves ppb to ppm sensitivity for a number of nitrocompounds, but is capable of significant increases in sensitivity with modifications to the lasers and sampling apparatus.

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IMPACT OF THE NEW CAA REGULATIONS  
ON THE DESIGN AND OPERATION OF  
AUTOMATED VOC SAMPLING INSTRUMENTATION

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**ABSTRACT**

Recent (1990) CAA Amendments and subsequent additions under Section 112 that set standards for 189 hazardous air pollutants require sampling and analysis of this expanded list of air toxics. This in turn poses new challenges to the available sampling equipment. While existing instruments continue to be a viable avenue, new hardware and even more refined sampling techniques will be needed. Continuously sampling automated samplers, manual systems, in-situ continuous analyzers and other techniques (as they become validated) will be considered for the future sampling projects. Multi-purpose automated VOC samplers will provide a viable approach based on many years of successful use of manual or automated single sample systems. Expected requirements for continuous or intermittent sampling for periods ranging from 1 to 8 hours during required 24 hr intervals dictate deployment of state-of-the-art sampling instrumentation. This paper will describe in some detail the design and performance of a new generation of automated multi-station VOC samplers.

**INTRODUCTION**

The gradual implementation of requirements for continuous monitoring of hazardous air pollutants results in a need for acceptable sampling and analytical procedures. The 1988 introduction of the EPA Method TO-14 outlined the basic parameters and hardware needs for sampling of the short list of VOC's. Five years later the needs far outstrip the capabilities of the existing instrumentation. Around the clock, integrated sample collection and/or analysis in one or more locations in a multitude of environments place great demands on the personnel and the instrumentation they use. Several recently introduced approaches exist, such as use of in-situ, automated GC or GC/MS analytical systems, remote sensors (IR, laser, microwave) or other alternate methods currently under investigation. This paper will concentrate on the evolution of the Method TO-14 instrumentation by utilizing state-of-the-art microprocessor technology that permits automated multi-mode sampling of VOC's.

**EXPERIMENTAL**

Early manual sample collection proved the value of Summa passivated sampling containers for both the qualitative and quantitative work in monitoring VOC's. As the demands for quality and frequency of sampling increased some degree of automation was needed. Mechanical, and later digital timers and electrically actuated valves eased the workload and commitments of field personnel. Holdren et al. (1) and Krasnec (2) described two automated VOC multi-container sampling systems in 1989. Several commercially available

systems were also introduced, but mostly for single container sampling. As the requirements for sampling of non-polar, polar (oxygenated/carbonyl group) and semi-volatile hydrocarbons increase so does the complexity of the sampling hardware. Additional requirements in the Ozone Non-Attainment Areas for sampling of the ozone precursors resulted in the establishment of a PAM (Photochemical Assessment Monitoring) network. Because a number of stations are already established and more are coming on-line the need for advanced VOC sampling equipment has greatly increased.

#### VOC Sampler Considerations

The task of collecting multiple samples in a given 24 hour period with reliability, flexibility and cost-effectiveness clearly dictates a need for highly automated, unattended sampling instruments. The reliance on mechanical and digital timers no longer satisfies the need for control, sampling monitoring and data gathering functions. Earlier designs that used small hand-held microcomputers showed promising performance but also some drawbacks (3) such as sensitivity to environmental effects (temperature, vibration/shock, electromagnetic fields, etc.), operator errors, power supply variations and others. Use of standard PC's or even laptop and notebook size PC's is possible but not ideal because of the cost, difficulty of use, software availability and user training limitations.

A survey of available electronics, and prototype evaluation in 1991 led S.I.S. to a full-time effort to design and build a microprocessor (microcontroller) controlled multi-station VOC sampler. The major innovation lies in the use of a dedicated microprocessor with a built-in real time clock/timer, 32K RAM and 12 MHz operating speed. While not as powerful as the latest computers on the market, the microprocessor handles the operation and control of the sampler hardware very efficiently. It controls up to sixteen latching solenoid valves, two pumps, up to two mass flow meters/mass flow controllers and several relays. In addition, the microprocessor will interface with and control external devices such as pressure transducers, temperature and wind speed/wind direction sensors, and it will facilitate remote operation via a modem and a built-in RS-232 interface. Further features of the microprocessor are its ability to control the entire sampler operation, including the sample sequencing, sampling cycle monitoring and sampling parameter storage, display and transfer to external devices, i.e. PC's. Recent work with preproduction samplers resulted in further enhancements. The most important are the ability to "re-cycle" after a power failure and to resume its original sampling sequence. Another feature is a self-calibration ability for the built-in mass flow meter or mass flow controller. Both Span and Zero functions can be monitored during the sampling cycle and calibration corrections implemented while the actual sampling takes place. This, of course, is much more desirable than the tedious and unreliable post-sampling calibration and corrections. Fleil (4) reported that electronic mass flow devices are subject to ambient temperature changes, vibration and other more subtle environmental variations. The microprocessor continuously monitors the sample flow, displays it or alternately provides an output to an external device. At the end of the sampling cycle it averages the flow over the entire sampling period and provides the TOTAL SAMPLE VOLUME. Thus, the self-calibration feature is indeed quite desirable.

Some of the additional features are the electronic duty-cycle control (choice of sampling from 1 to 100 % of the preset time period), elapsed (operating) time monitoring, sampling time count-down, display of real-time and sampling/purge time intervals. Post sampling cycle data is displayed on a large

two line LCD. It includes start time, sampling end time, power interruptions, number of samples collected (sampling times for each sample can be the same or individually set), duty cycle setting (if selected), elapsed time and the sample flow/volume parameters described above. The microprocessor also monitors and displays ambient (sampler) temperature. This feature allows electronic minimum/maximum temperature recording for the sampling record or an additional input for the sampler "self-calibration" function. Installation of an optional pressure transducer is possible for either monitoring ambient air pressure or sample stream pressure. The microprocessor controlled temperature sensor is also used to regulate the temperature of the sampler enclosure. This is done through activation of the internal cooling fan or the heating element. Additional features, such as the sample inlet and/or sample manifold heating can be incorporated. No mechanical thermostats with their inherent operational hysteresis are used.

These features can be utilized when sampling on solid adsorbents, SepPak, or PUF (PolyUrethane Foam) cartridges. Possibly the greatest advantage of the microprocessor control is its inherent ease for alternate modes of sampling (Summa container, solid adsorbent tube, or cartridge). Only relatively minor changes in the operating software are required when switching between different modes of sampling. It is entirely feasible to build a multi-mode sampler, i.e. Summa container and adsorbent tube, or Summa container and PUF cartridge, etc. version. Of course, the provisions for the proper hardware components (pumps, valves, flow meters and the sampling media) will have to be made at the time of the sampler construction.

The microprocessor programming language (FORTH) is available to users in the air sampling community. It is expected that the equipment manufacturer and some of the larger user organizations will have the in-house programming and software modification capability. The samplers do have a built-in RS-232 interface so that any standard or a compact notebook-size PC can be used for software loading, modifications, data retrieval and storage and subsequent sampling report preparation. On the field-user level no programming or even computer "literacy" is required. All sampling parameter set-up is done in response to microprocessor prompts. For example, setting sample starting time requires only that the operator responds to prompts to set the sampling month, day/date, minute and second individually, and entering these parameters into the unit. Typically, set-up of a sampling cycle takes less than five minutes. Once it is completed, the user has an opportunity to review the sampling parameters and to make corrections, if so desired. After this step, a single command activates the sampler, and a count-down time to sampling start is displayed. The actual sampling can begin hours or days later. Prior to sampling start all valves are closed to prevent system contamination. In the event of power failure or other sampling interruption the sampler software resets the sampler and isolates the sampling media from contact with the atmosphere. After the sampling resumes the system is stabilized for a preset period of time. Then, the originally set purge period follows. Only after this step does the actual sampling resume. The time of the sampling interruption is recorded and reported at the end of the sampling cycle.

The user accessible software is divided into a number of menu sections and subroutines. For example, the OPERATE menu allows access to the sampling PROGRAM subroutine. The UTILITY subroutine provides access to the valve and pump functions, or diagnostic functions. The REPORT subroutine gives all previously used sampling parameters. Another sections (VARIABLES) is used for setting important system parameters (rather than the routinely changed sampling parameters). This section also offers the calibration feature and is accessed only through a special code to protect the sampler from unauthorized use.

### VOC Sampler Construction

Typical microprocessor controlled sampler configuration consists of the sampler control module housed separately from the sample media module. When used with the Summa passivated SS sampling containers this module houses up to four 6 liter size containers. Additional two- or four-container modules can be added as needed (Fig. 1.). All sample path components are stainless steel with Viton seals (O-rings or diaphragms). The sample module is equipped with a manifold that permits individual connections to sampling containers. Each container has a separate on/off latching solenoid valve. The sampler is equipped with an inert sampling pump; flow control hardware (mechanical flow controller and a mass flow meter; or a mass flow controller); sample and pump pressure gauges, sample system pressure control valve and several ports with on/off latching solenoid valves. All controls, including the microprocessor LC display, control key-pad, pressure gauge displays and flow control adjustments are mounted on the horizontal control module panel. The mass flow meter display and control is via the microprocessor and its LCD. No separate control and power module is required. The built-in solid state 12V DC power supply allows operation from a rechargeable 12V DC battery, or from a regular 115V AC source.

A multi-tube adsorbent sampler configuration has been also investigated. Up to twelve adsorbent tubes are placed horizontally, side by side on the top of the control module. Each tube is equipped with a separate inlet on/off solenoid valve (Fig. 2.). An optional outlet valve assembly will also be available. All adsorbent tubes have a common inlet and outlet manifold. A sampling pump is located downstream from the tubes rather than upstream as was the case with the sampling containers. A flow controller and a mass flow meter are installed in the sample stream path. Again, the pre-set sample flow, actual average sample flow and the total volume of sampled air for each adsorbent tube is provided by the microprocessor. Similarly, all sampling parameter set-up, monitoring and sampling cycle data are displayed, stored and retrieved in the same fashion as with the Summa container sampler. A sample purge function is provided to allow system purge and conditioning. The installation and replacement of the adsorbent tubes is facilitated with the use of mounting clips, quick-connects and flexible SS tubing connection(s) to the sampling manifold.

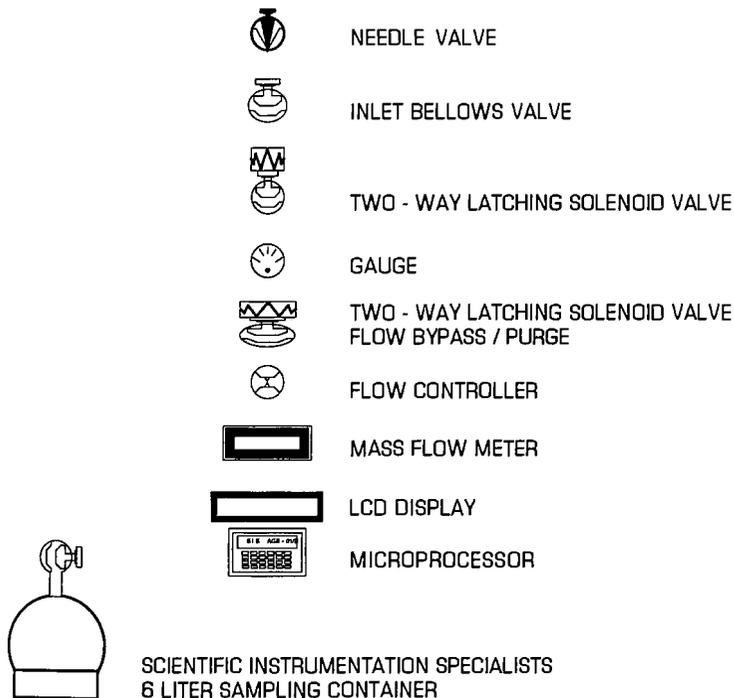
It is anticipated that a modification of the above configuration can be made for use with up to eight cartridges. Because of the greater pressure drop caused by increased flow resistance, a more powerful pump installation is proposed. In addition, a heated inlet line and inlet manifold zone may be required. Also, an ozone scrubber installation needs to be considered. A feasibility study for the modification of the above described adsorbent tube sampler to a microprocessor controlled cartridge sampler is planned for the near future.

### CONCLUSIONS

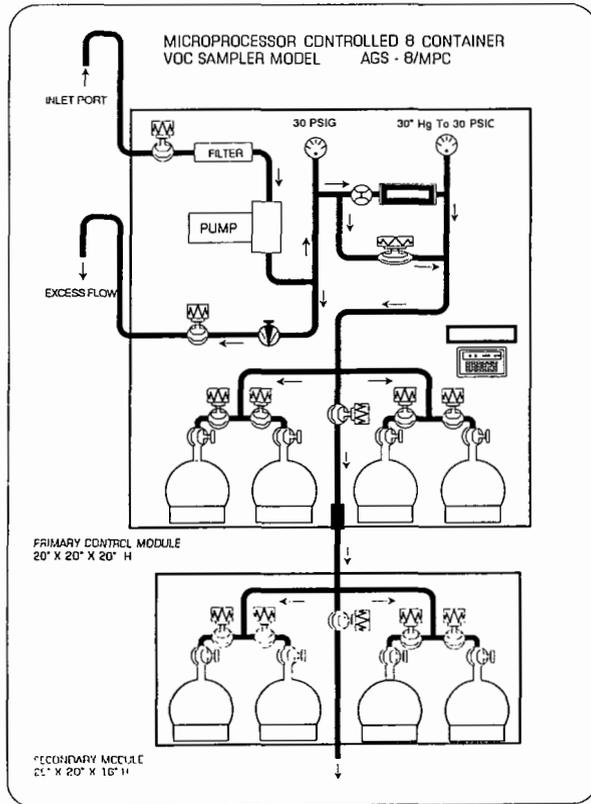
The introduction of microprocessor controlled VOC samplers provides a significant qualitative and quantitative step for use in the currently implemented 1990 CAA Amendments and Section 112 Additions. Further requirements for the PAM network, and needs of the ozone non-attainment areas for continuous sampling of VOC's clearly underline the need for versatile, highly automated and reliable sampling instrumentation. The flexibility and viability of the microprocessor controlled sampler has been demonstrated. Its multi-mode sampling capability and flexibility for collecting integrated 1 hour to 24 hour samples needs to be demonstrated in field use, and compared to other VOC monitoring methods.

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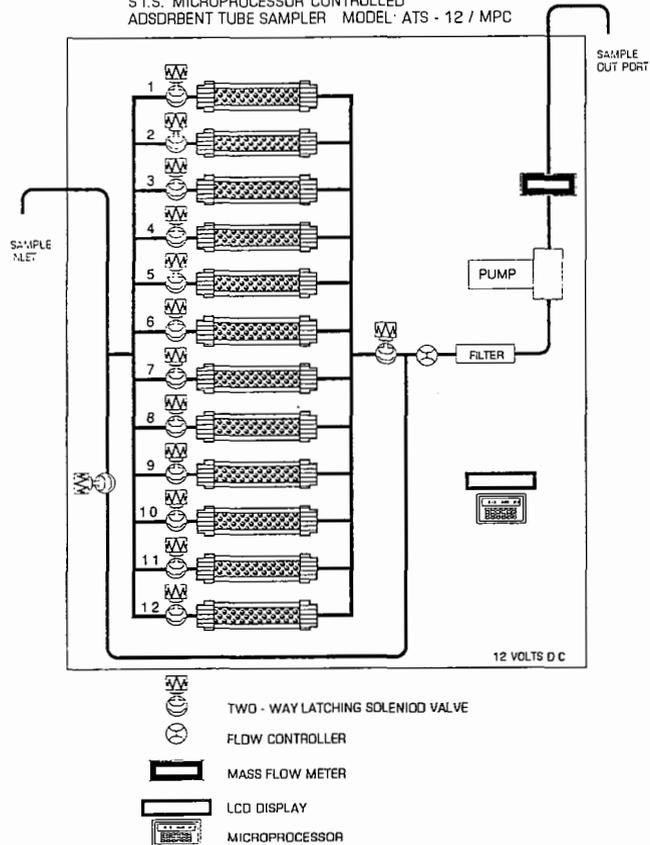
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Legend for Figure 1.



**S.I.S. MICROPROCESSOR CONTROLLED  
ADSORBENT TUBE SAMPLER MODEL: ATS - 12 / MPC**



## PRESSURE AND TEMPERATURE EFFECTS ON CONCENTRATION OF GASEOUS CALIBRATION STANDARDS

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### ABSTRACT

It is well-known that the concentration of gaseous calibration standards may be affected by the pressure and temperature of the standard. For example, if the component of interest has a low vapor pressure it may condense out of a standard prepared at too high a pressure or exposed to too low a temperature. On the other hand, very low concentration cylinder standards are usually only considered reliable if a certain minimum pressure remains in the cylinder. The maximum allowable concentration before condensation occurs in a standard can be calculated from thermodynamics, taking into account non-idealities at high pressures, as will be described. Although this calculation is straightforward enough from a fundamental point-of-view, it is not always understood in practice and it is necessary to estimate key parameters for many species currently of interest in environmental monitoring.

For many systems, it is not sufficient to consider condensation but one must also take adsorption-desorption phenomena into account. The pressure dependence of these phenomena is less well understood but a model has recently been proposed by Li et al. The implications of this model for cylinder standards will be discussed.

### INTRODUCTION

In order to make meaningful analyses of trace atmospheric pollutants, it is essential to have good calibration standards. Compressed gas mixtures in cylinders are widely used for this purpose because they are convenient, robust and well-characterized. As the range of pollutants of interest increases, more compounds are added whose stability in cylinders requires special care on the part of the standard manufacturer. It is important that the user of these standards have some understanding of factors influencing the concentration of impurities in calibration standards in order to consistently achieve the performance they require. In this paper we will briefly review some important fundamentals of vapor-liquid equilibria (VLE) and then move on to more recent work in the area of gas-surface interactions in cylinders. Some of the considerations which will be discussed in this paper for the case of cylinders, are also relevant to air samples collected in canisters, although those are generally at much lower pressures.

### CONDENSATION QUESTIONS IN CYLINDER GASES

As the number of molecules of any component in a gaseous calibration standard is increased, a condensed phase will eventually form and limit the gas phase concentration from increasing further. Gaseous standards are usually prepared in a manner which ensures that only gas phase species are present as otherwise the concentration in the gas phase will change dramatically as the cylinder is emptied.

The simplest attempt to calculate the maximum concentration of an component which can exist in a purely gas phase mixture is to ratio the vapor pressure of the component of interest to the total pressure in the cylinder. This type of calculation predicts that the maximum possible concentration in a cylinder decreases monotonically as the pressure increases, or, to put it another way, that the dew-point of a mixture will increase monotonically with temperature. For cylinder gases, however, it is necessary to allow for the effects of interactions of the matrix gas with impurities. Such interactions can be rather large at high pressures. Recall that the Critical Temperature of Nitrogen is  $-147^{\circ}\text{C}$  and that its Critical Pressure is 493 psia, which means that nitrogen in a typical gas cylinder is in a supercritical condition and thus

should often be considered as a solvent rather than as an inert matrix in which the organic molecules of interest are situated.

If we use the thermodynamic concept of *fugacity* (which is closely related to chemical potential), the fugacity of component  $i$  ( $f_i$ ) must be equal in all phases, i.e.

$$f_i^{liquid} = f_i^{gas} \quad (1)$$

from which it can be shown<sup>1</sup> that the mole fraction of component  $i$ ,  $y_i$ , in the gas phase is given by

$$y_i = \frac{P_i^{sat}}{P} \cdot \frac{x_i \gamma_i \phi_i^{sat}}{\phi_i^{apor}} \cdot \exp \int_{P_i^{sat}}^P \frac{v_L}{RT} dP \quad (2)$$

where the ratio of the saturated vapor pressure of component  $i$  to the total pressure,  $P_i^{sat}/P$ , is multiplied by an "enhancement factor" which is usually greater than one. The exponential term is known as the Poynting correction and takes into account the change in free energy of a condensed phase of molar volume  $v_L$  due to its being at pressure  $P$  rather than the saturated vapor pressure. It is usually between 1 and 3.  $x_i$  is the mole fraction of  $i$  in the condensed phase and will be close to 1 if component  $i$  is the least volatile present. The fugacity coefficients,  $\phi$ , are defined by

$$f_i^{sat} = \phi_i^{sat} P_i^{sat}$$

$$f_i^{apor} = y_i \phi_i^{apor} P$$

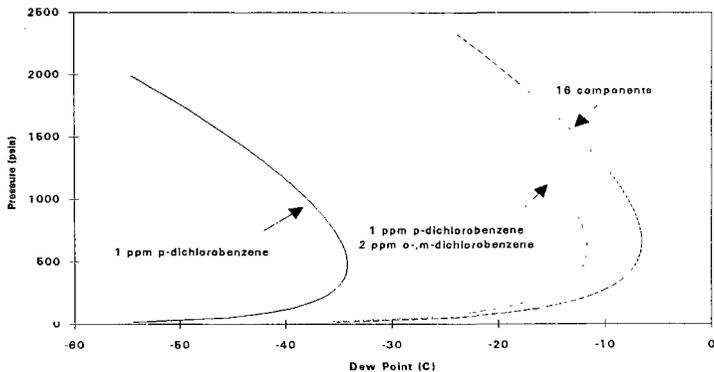
$\phi_i^{sat}$  accounts for the non-ideality of the saturated vapor and, as we are by definition dealing with impurities of low vapor pressure, is usually close to 1.  $\phi_i^{apor}$  is the fugacity coefficient of the component of interest in the vapor phase and is responsible for large enhancement effects (up to several orders of magnitude).

$\gamma_i$  is the activity coefficient of component  $i$  in the condensed phase. If the condensed phase is pure, then  $\gamma_i = 1$ , otherwise  $\gamma_i$  provides a measure of the interactions between organic species in multicomponent mixtures. This is the **only** factor which is likely to result in a **reduction** of the actual concentration with respect to the ratio  $P_i^{sat}/P$ . For example, if one component were present at a concentration which was high relative to its vapor pressure, not only might it condense, but other components might dissolve in it, with the result that their concentrations would also be lower than expected.

Equation (2) is useful for calculations below the critical point and allows useful indicators of the direction of expected trends to be derived. In practice, however, activity coefficients are not available at high pressures and other complications arise. It is therefore more effective to use an equation of state which can describe both the liquid and the gas phase and solve Equation (1) directly. Many such equations exist (such as the Soave-Redlich-Kwong (SRK) and Peng-Robinson equations) and computer programs capable of carrying out the calculations are readily available. Sometimes it is necessary to estimate parameters necessary for the description of more unusual organic molecules or species which are not important in the chemical industry (where VLE calculations are used extensively).

#### Application to practical mixtures

It is interesting to note that equation of state calculations such as those discussed above are able to take interference effects between compounds into account reasonably well. *p*-Dichlorobenzene is a solid organic compound: It is included at 1 ppm in a 41-component mixture sold for TO-14 analyses. The other components of that mixture are present at 2 ppm and cover a wide range of volatility, but *p*-dichlorobenzene is the least volatile. Figure 1 illustrates the application of VLE calculations to several mixtures containing 1 ppm (by volume) *p*-dichlorobenzene in balance nitrogen. The data are presented



**Figure 1:** Dew Point Curves calculated using the SRK equation of state. Results are shown for the following mixtures in Nitrogen: 1 ppm p-dichlorobenzene, 1 ppm p-dichlorobenzene 2 ppm each o-,p-dichlorobenzene, 1 ppm p-dichlorobenzene, 2 ppm each o-,m-dichlorobenzene, 1,2,4-trimethylbenzene, p-ethyl-toluene, o-,m-,p-xylene, ethylbenzene, 1,1,2,2-tetrachloroethane, styrene, 1,1,2-trichloroethane, toluene, benzene and chlorobenzene.

in the form of a plot of dew point of the mixture as a function of cylinder pressure. The dew point increases with pressure at low pressure, as expected, goes through a maximum and then decreases again. For a mixture containing only p-dichlorobenzene, the dew point never exceeds  $-30^{\circ}\text{C}$ . Including the other isomers of dichlorobenzene has a substantial effect on the dew point. Bringing the total number of components up to 16 by including more low-volatility compounds has a substantially smaller effect and as we work through the list of compounds in reverse order of elution (i.e. in order of increasing volatility), each additional compound has less effect on the dew point of the mixture.

#### Comparison with experimental results

The thermodynamic description of vapor-liquid equilibria reviewed above has been extensively verified in practice (see, for example, the examples in reference 1). In particular, the shape of the curves in Figure 1 is typical and similar behavior is observed for a wide range of compounds. However, gas-surface interactions in cylinders are much less well understood and their description does require proper incorporation of the effects of high pressure. With this in mind we prepared a set of mixtures which were deliberately designed to exhibit condensation effects at accessible temperatures. The composition range of the mixtures was 9-15 ppm benzene, toluene, p-dichlorobenzene, 40-75 ppm chlorobenzene. p-Dichlorobenzene, a solid compound of low volatility, was intentionally included at a relatively high concentration. This species is usually supplied at concentrations of 1 ppm or less. The concentration of chlorobenzene was sufficiently high that we could expect to describe its behavior reasonably well while neglecting gas-surface effects, at least at high pressure (see the next section). The mixtures were prepared in disposable "MedGas E" cylinders (supplied by Alphagaz) which are carbon steel.

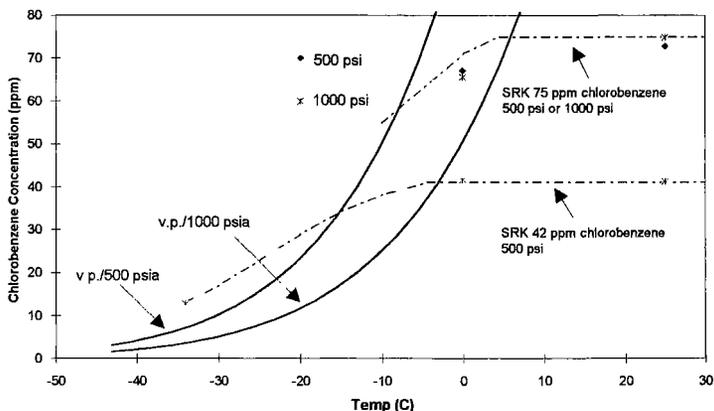
In order to observe condensation effects, even for these specially prepared mixtures, it is necessary to cool the cylinder. A range of cylinder temperatures was achieved by using ice or coolant baths. Figure 2 compares the results of several measurements made on these mixtures with the results of equation-of-state calculations using the Soave-Redlich-Kwong (SRK) equations. Curves based on the ratio of vapor pressure to cylinder pressure are also shown for the purpose of comparison.

For a cylinder containing 9 ppm each of benzene, toluene p-dichlorobenzene and 42 ppm chlorobenzene in a balance of 1000 psi nitrogen, excellent agreement is obtained with the SRK calculation, as shown in Figure 2. Note that the concentration at -34°C is substantially larger than predicted by simply dividing the vapor pressure by 1000psi, in accord with the discussion above.

In cases where a condensation problem is anticipated, one may be inclined to use a cylinder prepared at lower pressure in or "to be safe". This is not always advisable. In Figure 1, however, we see that a rather small difference in dew point can exist even though the cylinder pressure varies by a large factor (e.g. between 500 and 1000 psi). For the case of a cylinder prepared with 15 ppm each benzene, toluene, p-dichlorobenzene, 75 ppm chlorobenzene, the SRK equation-of-state calculation predicts a very small concentration difference between a 1000 psi cylinder and a cylinder at 500 psi. In Figure 2, these curves are superimposed and cannot be distinguished. A cylinder was prepared using the above composition at 1000psi and analyzed at 25°C and at 0°C. The lower temperature data showed a decrease in concentration. The cylinder was allowed to "blow down" to 500 psi at room temperature (using a sufficiently slow flow rate that no cooling occurred). The measured concentrations were the same as before at both temperatures, although one might have expected to avoid condensation at 0°C based on the curve labeled "vapor pressure/500 psia". The error bars (for one standard deviation) on the experimental data are approximately the same size as the point markers in the figure, so the SRK calculation is significantly higher than the observed values at 0°C, but correctly predicts the trend and is substantially closer to the observed values than either vapor pressure ratio curve.. This is an example where the relatively high concentration of p-dichlorobenzene leads to condensation at 0°C and affects the concentration of chlorobenzene.

#### GAS-SURFACE EFFECTS

In practice, calibration standards for air analysis are generally prepared at compositions where condensation is not an issue. Indeed, from Figure 1, one might suppose that one could use many mixtures



**Figure 2:** SRK Equation of State Calculations for: (i) a mixture containing 9 ppm each benzene, toluene, p-dichlorobenzene, 42 ppm chlorobenzene in 1000 psia nitrogen balance (ii) a mixture containing 15 ppm each benzene, toluene, p-dichlorobenzene, 75 ppm chlorobenzene in 500 psia nitrogen and in 1000 psia nitrogen. Experimental data for both concentrations and for the 75 ppm chlorobenzene system at both pressures are indicated. The result of dividing the vapor pressure (v.p.) of chlorobenzene by 500 psia and by 1000 psia are included for comparison.

at temperatures below freezing without difficulty. Unfortunately, this is not the case because of the importance of gas surface effects. These can be broadly divided into two categories:

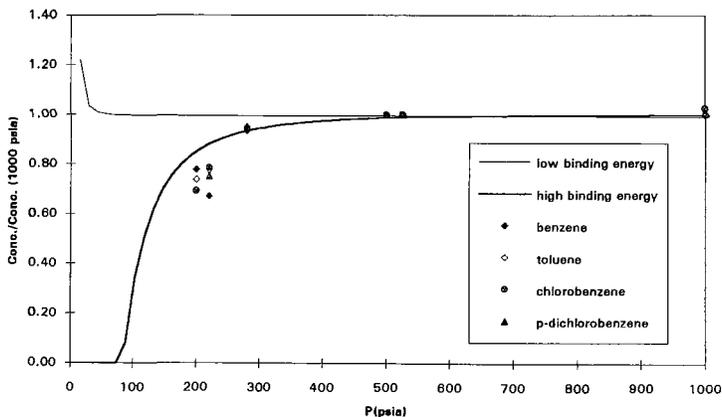
**Physisorption:** Molecules are bound to the surface by relatively weak physical forces which do not lead to breakage of any intra-molecular bonds

**Chemisorption:** Molecules are strongly bound to the surface and intra-molecular bonds may be broken. The distinction is important in practice because physisorption is reversible: for example, if a cylinder is exposed to extremely low temperature in storage, some fraction of the impurity molecules may be physisorbed, but once the cylinder is restored to a more appropriate temperature the original impurity concentration will be recovered (provided no substantial amount of gas is withdrawn while the cylinder is cold). Chemisorption, however, is more difficult to reverse. In order to make stable calibration standards it is necessary to properly prepare the gas cylinder so that the surface does not chemisorb the species of interest, or, more precisely, so that the number of available chemisorption sites is small compared to the number of available gas phase molecules. As the concentration of the calibration standard is reduced this becomes more difficult.

#### Model for Gas-Surface interactions in High Pressure Cylinders

Recently, Li et al.<sup>2</sup> incorporated the thermodynamic treatment of pressure effects on fugacity as described in the preceding section into a model which also allowed for adsorption on the cylinder walls according to a Langmuir isotherm. They applied this to the description of the pressure dependence of moisture concentration in cylinders of Ultra-High Purity (UHP) Nitrogen. The same model can be applied to organic species present in calibration standards.

When a cylinder of UHP gas is at full pressure, and if it was properly dried before filling, its moisture concentration is essentially that of the gas source used, which is usually very low. As the gas is depleted, the moisture concentration gradually rises due to desorption from the cylinder walls, usually with a sharp increase at some low pressure (about 100 psi). The detailed behavior depends on the cylinder material and on the procedure used to dry the cylinder. This behavior is correctly predicted by the model.



**Figure 3.** Effect of Adsorption-Desorption on the concentration of a gaseous calibration standard. The predictions of the model of Li et al are shown for two sets of gas-surface interaction parameters (see text). The "low binding energy" curve displays the behavior typically observed for moisture in a gas cylinder. Experimental data for the four aromatic species in mixtures (i) and (ii) discussed under Figure 1 are also shown. These mixtures were prepared in carbon-steel cylinders.

The adjustable parameters used by the model are the number of surface sites available and the equilibrium constant for surface adsorption. One of its more interesting features is that it predicts a *qualitatively* different pressure dependence of the concentration for different ranges of values for these parameters. This is illustrated in Figure 3. The effects of the two parameters are convoluted together and are difficult to completely separate. If the average gas-surface bond is weak or if the number of sites is small, then the concentration increases at low pressure, if the average bond is strong, or there are many sites, it decreases. As discussed above, moisture shows the typical "weak binding" behavior. When the series of cylinders discussed earlier were slowly reduced in pressure, they showed the opposite, strong binding, effect. The model's predictions are not in perfect agreement with experiment but it is clearly capable of reproducing qualitative features correctly. It is striking that the dependence is approximately the same for all four species despite a wide range of volatilities and the fact that chlorobenzene is present at approximately 5 times higher pressure than the other three species. These mixtures were prepared in carbon steel cylinders; mixtures prepared in aluminum cylinders show qualitatively the same behavior (in our experience), but the value of the pressure at which concentration starts to drop off may be somewhat lower.

#### **CONCLUSIONS AND PRACTICAL IMPLICATIONS.**

This discussion has been far from exhaustive and it should be remembered that other factors can come into play which were not mentioned here. One obvious candidate is reactions between impurities in the same calibration standard, but this can generally be avoided as most incompatibilities are understood. Molecules which tend to polymerize give rise to more difficult problems which often require an empirical approach to the selection of appropriate cylinder treatment, fill pressure and concentration.

In preparing standards, methods for establishing concentrations which will not lead to condensation problems are relatively well-established and require only access to suitable computer code and the ability to successfully estimate some parameters. Gas-surface interactions are less well understood, but a model capable of reproducing observed behavior exists and we can expect our understanding to develop. Generally speaking, mixtures at higher concentrations and higher pressures give rise to fewer problems. It is important not to use underestimate the pressure at which condensation will occur for a given mixture composition, as too low a pressure may give rise to problems due to surface effects.

In using calibration standards it is necessary to take reasonable precautions not to expose them to extremes of temperature or to deplete them to too low a pressure. If a cylinder is exposed to low temperature (below 40°F) it should be allowed to warm up before any gas is withdrawn. The cylinder should not be completely depleted as the concentration will vary. Avoiding pressures below 300 psi appears to provide a reasonable margin of safety.

#### **ACKNOWLEDGMENTS**

Thanks to Benjamin Jurcik for many useful conversations and instruction in the calculation of Vapor-Liquid-Equilibria. Thanks to Yao-En Li for explaining his model and providing the computer program embodying it which was prepared by Matt Giacobbe.

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***Session 24***

***General***

## LABORATORY EVALUATION OF GAS DILUTION SYSTEMS FOR ANALYZER CALIBRATION AND CALIBRATION GAS ANALYSIS

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### ABSTRACT

Gas dilution systems can be used for multipoint calibrations of pollutant gas analyzers and for the analysis and certification of compressed gas calibration standards. This laboratory evaluation obtained estimates of the accuracy and precision of four representative gas dilution systems. Diluted and undiluted gas mixtures containing carbon monoxide, nitric oxide or sulfur dioxide in nitrogen were sampled by pollutant gas analyzers. Accuracies were estimated from the difference between the slopes of regression lines from measurements of the diluted and undiluted gas mixtures. These accuracy estimates ranged from -3.3 to 10.0 percent. Precisions were estimated from the 95-percent uncertainty for regression-predicted concentrations. These precision estimates ranged from 0.3 to 14.9 percent of the predicted concentration for mid-range dilutions.

### INTRODUCTION

Calibration gases often are diluted during the multipoint calibration of pollutant gas analyzers and during the analysis and certification of compressed gas calibration standards. Gas dilution systems are devices that allow two gas streams to be mixed together continuously and quantitatively. Such systems could be used for multipoint calibrations and analyses of gas mixtures. However, systematic and random errors associated with the dilution would be added to the total measurement uncertainty. Could one use gas dilution systems for these applications with acceptable levels of accuracy and precision?

Under U.S. Environmental Protection Agency (EPA) sponsorship, Research Triangle Institute (RTI) conducted a laboratory evaluation of four representative gas dilution systems. The goal of the evaluation was to estimate the accuracies and precisions of the systems using measurements by pollutant gas analyzers. These estimates were obtained from the statistical analysis of multipoint calibrations using undiluted and diluted gas mixtures.

### GAS DILUTION SYSTEMS

The Enviro-nics Model 2020 continuous emissions monitoring calibration system uses thermal mass flow controllers to regulate the flow rates of a compressed gas calibration standard and dilution nitrogen, which are blended together. The system was configured to operate in both of the dilution regions that were used in the evaluation (i.e., 1 to 9 percent and 10 to 90 percent of the standard's concentration). Its specified flow rate accuracy is  $\pm 0.5$  percent of the full-scale range and its specified flow rate repeatability is  $\pm 0.2$  percent of the full-scale range.

The Milton Roy Model 821S gas divider uses 10 identical, parallel capillary tubes and solenoid valves to blend the calibration standard and the dilution nitrogen. The system was configured to operate in the 10 to 90 percent dilution region. Its specified dilution accuracy is  $\pm 0.2$  percent of the standard's concentration and its specified repeatability is  $\pm 0.1$  percent of the point.

The Wösthoff Model 1KM67 gas mixing pump uses 2 piston-driven, positive-displacement pumps to blend the calibration standard and the dilution nitrogen. The standard goes through one pump and the nitrogen goes through the other pump. Switchable gears vary the pistons' stroke frequency and thereby vary the diluted gas concentration. The pumps and gears in the instrument used for this evaluation were lubricated with silicone oil. The system was configured to operate in the 1 to 9 percent dilution region. Its specified accuracy under calibration conditions is  $\pm 1.0$  percent relative to the selected dilution level.

The Wösthoff Model 5KA37 gas mixing pump uses 5 piston-driven, positive-displacement pumps to blend the calibration standard and the dilution nitrogen. The pumps are an oilless type and have a fixed stroke frequency. Three stopcocks are used to switch the gas streams entering 3 of the 5 pumps and thereby vary the diluted gas concentration. The system was configured to operate in the 1 to 9 percent dilution region. Its specified accuracy under calibration conditions is  $\pm 0.5$  percent relative to the selected dilution level.

## EXPERIMENTAL PROCEDURES

Gas mixtures containing carbon monoxide (CO), nitric oxide (NO), or sulfur dioxide (SO<sub>2</sub>) in nitrogen were measured during the evaluation. These measurements were made using the analytical instrumentation listed in Table 1. Several gas dilution systems were compared within a single day's time. All measurements that were obtained on the same day were considered to be comparable and no measurements were compared across different days.

Multipoint calibrations were performed using undiluted and diluted gas mixtures. The undiluted gas mixtures were National Institute of Standards and Technology Standard Reference Materials (NIST SRMs) and zero-grade nitrogen. These gas mixtures were the reference standards for the accuracy estimates. The diluted gas mixtures were obtained by dilution of EPA Protocol Gases, which are prepared and analyzed by specialty gas producers using an EPA-specified protocol. RTI verified the certified concentrations of these standards relative to the concentrations of the SRMs.

The calibration data were analyzed using least-squares regression techniques under the assumption of a constant random error term. For several multipoint calibrations, a quadratic equation fitted the data better than a straight-line equation. The accuracy of the gas dilution systems was estimated by comparing the slope of the regression line for the diluted gas mixtures with the corresponding slope for the undiluted gas mixtures.

$$\text{Accuracy} = 100 \left[ \frac{\text{Diluted Slope} - \text{Undiluted Slope}}{\text{Undiluted Slope}} \right]$$

This value is constant across the range of predicted concentrations. Statistical tests were performed to check if the diluted slope was significantly different from the undiluted slope.

The precision of the gas dilution systems was estimated by the relative uncertainty of concentrations that are predicted from the regression equation.<sup>1</sup>

$$\text{Precision} = 100 \left[ \frac{95\text{-Percent Uncertainty for Predicted Conc.}}{\text{Predicted Concentration}} \right]$$

Although the 95-percent uncertainty is approximately constant across the range of predicted concentrations, the precision estimate varies inversely with the predicted concentration. This variation is illustrated in Table 2 which gives precision estimates obtained from the multipoint calibration of the NO analyzer on its 0 to 250 parts per million (ppm) range. The precision at the upper end of the regression line is approximately 0.5 percent, but the precision at the lower end is approximately 9 times larger. In this paper, precision estimates are generally listed for dilutions of 5 or 50 percent of the diluted standard's concentration.

The precision estimates also vary with the number of measurements in the multipoint calibration and with the number of measurements of the unknown sample. This variation is illustrated in Table 3, which gives precision estimates obtained from various subsets of the 250 ppm NO multipoint calibration. The precision estimates for a 5-point calibration and 1 sample measurement are approximately 2 to 3 times larger than the precision estimate for a 10-point calibration and 3 sample measurements. This example demonstrates that precision estimates can be improved by increasing the number of measurements.

Several unexpected events occurred during the evaluation. Excessive zero drift in the NO analyzer was discovered and repaired. Several days' data were discarded because of this zero drift. One of the capillaries in the Milton Roy 821S system became plugged during the evaluation and this system could no longer be used. The slope of the diluted SO<sub>2</sub> regression line for the Wösthoff 1KM67 system was significantly different from the slopes of the undiluted gas mixtures and the other systems' diluted gas mixtures. This difference may be due to interference of silicone oil from the Wösthoff 1KM67 system on the ultraviolet fluorescence SO<sub>2</sub> analyzer. Additionally, oil was seen coming from the system's nitrogen pump and a dropout trap was installed to prevent downstream oil contamination. Worse than expected precision estimates for the Wösthoff 5KA37 system prompted its inspection and repair by its manufacturer. A minor leak was discovered and the system was reevaluated at RTI after it was repaired.

## RESULTS

Several caveats concerning the evaluation should be considered as the results are reviewed. The evaluation studied only a limited range of experimental conditions. The evaluation did not attempt to obtain optimum performance (e.g., better precision estimates) from the gas dilution systems due to time constraints on experiments. Not all of the gas dilution systems were evaluated in the same dilution region. The gas dilution systems that were evaluated were selected based only on their availability and their dilution principles. The evaluation did not assess the corresponding accuracy and precision of undiluted gas mixtures which might be used in multipoint calibrations.

The results of the evaluation are given in Table 4 for the Enviro-nics and Milton Roy systems at the higher-concentration dilutions (i.e., 10 to 90 percent of the standard concentration). The results for the SO<sub>2</sub> and CO multipoint calibrations are given for both straight-line and quadratic regressions. The SO<sub>2</sub> analyzer is slightly nonlinear and the CO analyzer is quite nonlinear. Accuracy estimates were not calculated for the quadratic regressions. The Milton Roy 821S system was not evaluated beyond the NO and SO<sub>2</sub> calibrations because of the plugged capillary.

The results of the evaluation are given in Table 5 for the Enviro-nics and Wösthoff systems at the lower-concentration dilutions (i.e., 1 to 9 percent of the standard concentration). Results are given for the Wösthoff 5KA37 system both before and after its repair. The last two after-repair accuracy estimates may be biased due to a concentration shift in the SRM associated with low cylinder pressure. The SO<sub>2</sub> calibration was replicated to verify the slope accuracy estimate for the Wösthoff 1KM67 system.

**CONCLUSIONS**

The number of experiments conducted in the evaluation is too small to allow one to draw any firm conclusions concerning the accuracy of the gas dilution systems. For 12 of the 25 accuracy estimates, there was no statistically significant difference between the slopes of the regression lines for the undiluted and diluted gas mixtures. The values of the remaining 13 accuracy estimates ranged from -4.5 to 10.0 percent although the extreme values are associated with a nonlinear calibration curve and a possible interference effect. The accuracy estimates exhibit some variations from one day to the next and from one experimental condition to the next. In general, the accuracy estimates for the four gas dilution systems were similar.

The precision estimates for the four gas dilution systems were also generally similar. The values range from 0.3 to 14.9 percent for predicted concentrations in the middle portion of the regression line. The largest values are associated with a leaking system. The precision estimates exhibited some variations from one day to the next and from one experimental condition to the next. The precision estimates were significantly different in different portions of the regression line. Better precision can be obtained by making more measurements during multipoint calibrations and sample measurements.

**DISCLAIMER**

Although the research described in this paper has been funded wholly by the U.S. EPA through Contract No. 68-D1-009 to RTI, 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.

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Table 1. Analytical instrumentation for laboratory evaluation of gas dilution systems.

Gas Mixture	Pollutant Gas Analyzer	Analyzer Range (ppm)	
		For Dilution of 10% to 90% of Std. Conc.	For dilution of 1% to 9% of Std. Conc.
CO/N <sub>2</sub>	Bendix 8501-5CA	1000	50
NO/N <sub>2</sub>	Thermo Electron 10AR	250	25 and 100
	Columbia Scientific 1600	--	5
SO <sub>2</sub> /N <sub>2</sub>	Thermo Electron 40	500	50

Table 2. Comparison of precision estimates associated with different predicted concentrations for the same multipoint calibration.

NO Analyzer Range (PPM)	Gas Dilution System	Precision (percent)		
		At Dilution of 90% of Std. Conc.	At Dilution of 50% of Std. Conc.	At Dilution of 20% of Std. Conc.
250	Enviroics 2020	0.59	0.97	5.14
	Milton Roy 821S	0.50	0.85	4.53

Table 3. Comparison of precision estimates associated with various number of measurements of calibration standards and sample.<sup>a,b</sup>

Measured Values Used in the Regression Calculations	No. of Values in Regression	Precision at Dilution of 50% of Std. Conc.	
		1 Sample Measurement	3 Sample Measurements
Odd Values <sup>c</sup>	5	1.85	1.24
Even Values <sup>d</sup>	5	1.20	0.81
All Values	10	0.97	0.61

<sup>a</sup>Gas dilution system Enviroics 2020

<sup>b</sup>Analyzer range 250 ppm NO

<sup>c</sup>Odd values 10, 30, 50, 70, 90% of std. conc.

<sup>d</sup>Even values 0, 20, 40, 60, 80% of std. conc.

Table 4. Results for higher concentration dilutions (10 to 90 percent of standard concentration).

Gas Mixture	Analyzer Range (PPM)	Gas Dilution System	Slope Accuracy (Percent)	Precision at Dilution of 50% of Std. Conc.
NO/N <sub>2</sub>	250	Enviroics 2020	1.60	0.97
		Milton Roy 821S	0.25	0.85
SO <sub>2</sub> /N <sub>2</sub>	500	Enviroics 2020	2.50 <sup>a</sup>	1.24
		Milton Roy 821S	0.74	2.38
SO <sub>2</sub> /N <sub>2</sub> <sup>b</sup>	500	Enviroics 2020	----	0.76
		Milton Roy 821S	----	2.12
CO/N <sub>2</sub>	1000	Enviroics 2020	-4.53 <sup>a</sup>	10.90
CO/N <sub>2</sub> <sup>b</sup>	1000	Enviroics 2020	----	0.47

<sup>a</sup> Statistically significant difference between diluted and undiluted slopes

<sup>b</sup> Quadratic regression

Table 5. Results for lower concentration dilutions (1 to 9 percent of standard concentration).

Gas Mixture	Analyzer Range (PPM)	Gas Dilution System	Slope Accuracy (Percent)	Precision at Dilution of 5% of Std. Conc.
NO/N <sub>2</sub>	100	Enviroics 2020	-0.72	1.01
		Wösthoff 1KM67	-0.53	1.05
		Wösthoff 15KA37	-0.43	14.48
NO/N <sub>2</sub> (after repair)	100	Wösthoff 5KA37	1.25 <sup>a</sup>	1.52
		Wösthoff 5KA37	0.98 <sup>a</sup>	1.39
		Wösthoff 5KA37	1.08 <sup>a</sup>	2.13
		Wösthoff 5KA37	2.17 <sup>a</sup>	1.38
		Wösthoff 5KA37	2.11 <sup>a</sup>	1.59
NO/N <sub>2</sub> <sup>b</sup>	5	Enviroics 2020	1.39 <sup>a</sup>	0.31
		Wösthoff 1KM67	0.11	0.59
		Wösthoff 5KA37	0.34	12.64
SO <sub>2</sub> /N <sub>2</sub>	50	Enviroics 2020	2.62 <sup>a</sup>	3.13
		Wösthoff 1KM67 <sup>c</sup>	9.87 <sup>a</sup>	3.81
		Wösthoff 5KA37	0.51	14.91
SO <sub>2</sub> /N <sub>2</sub>	50	Enviroics 2020	-1.97	2.08
		Wösthoff 1KM67 <sup>c</sup>	10.04 <sup>a</sup>	5.22
		Wösthoff 5KA37	-1.52	12.28
CO/N <sub>2</sub>	50	Enviroics 2020	-3.33 <sup>a</sup>	0.74
		Wösthoff 1KM67	-0.90 <sup>a</sup>	1.11
		Wösthoff 5KA37	1.09	9.75

<sup>a</sup> Statistically significant difference between diluted and undiluted slopes

<sup>b</sup> Reference standard was diluted for these measurements

<sup>c</sup> Possible interference effect from silicone oil

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## A DUAL PURGE & TRAP / AIR TOXICS PRECONCENTRATION SYSTEM FOR 16-POSITION GC/MS ANALYSIS OF CANISTERS, WATERS, AND SOILS.

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### ABSTRACT

In order to achieve the necessary detection limits for the EPA 500 Series drinking water methods and ambient Air Toxics monitoring using EPA Method TO14, the preconcentrators and GC/MS systems utilized must be optimized. This usually includes implementing a direct coupling of the analytical column to the mass spectrometer to insure that the entire sample is introduced into the source. Due to the 1-2 ml/min limitation of current benchtop mass spectrometers, an on-column focusing stage is generally incorporated to further reduce the sample volume for improved chromatography of the lighter target analytes.

An Entech 2000 preconcentrator has been modified to allow its focusing trap to be used for focusing both canister samples and purge and trap samples. Full contact communication is provided to an OI 4560 Purge and Trap with 16-position manifold to allow unattended operation. The interface also permits full use of the GC injector allowing a convenient way to introduce standards, BFB, and high concentration air samples. The GC injector and purge and trap are connected in series before the focusing trap on the Entech 2000 therefore eliminating the need for Y connectors and splitters. The system can be set up to switch automatically from waters or soils to canisters after all preprogrammed positions are completed.

### INSTRUMENTATION

A diagram of the system is shown in FIGURE 1. A Hewlett-Packard 5890 Series II GC with EPC was interfaced to an OI 4560 Purge and Trap by connecting 1/16" nickel 200 tubing to the bottom of the injector to deliver the GC carrier directly into the 6-port rotary valve on the purge and trap. The 1/16" tubing was heated to allow heavy VOC's to be introduced at the GC injector (BFB, ppm standards and samples, etc.). The standard heated transfer line from the purge and trap was routed directly into port 4 of the Entech 2000 Automated Preconcentrator 8-port rotary valve allowing on-column focusing. The standard heated transfer line from the Entech 2000 was then connected to the analytical column in the 5890 GC oven using a zero dead volume union.

Purge and Trap of both waters and soils was performed using a multibed VOCARB trap from Supelco (Bellefonte, PA) allowing samples to be both quantitatively trapped and efficiently

dry-purged before desorption to the 2000 Preconcentrator. Focusing was performed on a deactivated, uncoated megabore column (0.53mm ID) at temperatures below -170 deg. C followed by a 10,000 deg. C per minute initial temperature ramp upon injection to maintain narrow peak widths. Separations in the GC were accomplished on a J&W 60m DB5 column (0.32mm ID, 1um film) using a 35 deg. C starting oven temperature.

Communication between the GC, Purge and Trap, and 2000 Preconcentrator was performed using contact closures. Rather than implementing the classical approach of using the oven ready signal to start sample desorption from the purge and trap, the Aux Out signal from the Entech 2000 was used to indicate when the focusing trap was cold and ready to accept the desorbed sample. The focusing trap, in turn, cooled only when both the sample list in the 2000 controller software indicated that another sample remained to be focused and when the GC ready signal was obtained. The overall operation is described in the flow chart in FIGURE 2.

## DISCUSSION

The described system uses a totally new approach for interfacing the GC carrier gas to both a Purge and Trap and Air Toxics preconcentrator. Instead of teeing these systems in parallel, each component is placed in a loop in series. The GC carrier first passes through the injector where sample could be introduced manually, allowing direct BFB injections. Source level samples could also be introduced using gas-tight syringes when higher VOC concentrations require 0.1 - 2.0 cc sample volumes. The GC carrier is then accessed at the bottom of the injector to deliver the regulated helium directly into the heated rotary valve on the purge and trap. Connection at the bottom of the injector eliminates the usual modifications of the GC (GC/MS) flow regulation pneumatics thereby allowing much easier interfacing to sophisticated flow/pressure controllers such as Hewlett-Packard's Electronic Pressure Control (EPC). In addition, bypassing of the entire purge and trap/Air Toxics inlet for troubleshooting purposes is easily accomplished by removing the transfer line at the bottom of the injector and replacing it with the analytical column.

From there, the GC carrier gas is routed to the purge and trap for VOC recovery from the sorbent trap when requested. Adequate focusing times during trap desorption are dependent on GC carrier flow rates and are fully adjustable through the Entech control software. For a flow rate of 1.5cc/min, 4 minutes worked well. Desorption of the focusing trap occurs very rapidly providing the narrow peaks given in figures 3 and 4. Both chloromethane and vinylchloride are shown to have gaussian peak shapes indicating that no dead volume was experienced during the injection. Peak widths for these early eluters were comparable to those of analytes eluting later in the analysis.

Finally, the GC carrier is introduced directly into the 8-port valve in the 2000 Preconcentrator to also permit introduction of VOC's obtained from air samples into the focusing trap. Canisters and tubes are first concentrated in modules 1 and 2 before backflushing into the focusing trap.

## CONCLUSIONS

A new Air Toxics/P&T/GCMS interface has been demonstrated that serially connects multiple inlets into the GC carrier flow path before a final focusing stage. Some of the advantages realized with such an approach include:

1. No hardware changes necessary when switching from purge and trap to canisters or tubes.
2. Provides maximum utilization of GC/MS hardware and data systems.
3. Permits laboratories to work their way into the air market at lower initial costs by time sharing a GC/MS with purge and trap, canister, and tube autosamplers.
4. Provides better sensitivity and resolution of lighter VOC's in water and soil analysis.
5. Forces all retention times and peak shapes to be identical for a given analyte no matter which inlet the analyte was introduced from (common focus point).
6. Allows a convenient way to check method recoveries by P&T and TO14 by comparing responses to direct injection of concentrated (or methanol) standards.
7. Focusing is performed after the injector so typical peak broadening that would occur therein are not present.
8. The novel design of the Entech 2000 Preconcentrator focusing trap allows it to operate on about 50 cents worth of liquid nitrogen per analysis.

# "Software" Selection of Canister, Tube, Water or Soil Sample Types

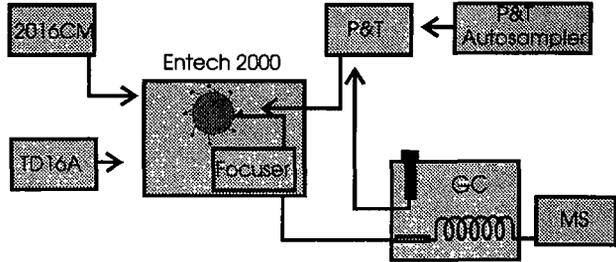


FIG 1

## Control of P&T by Entech 2000

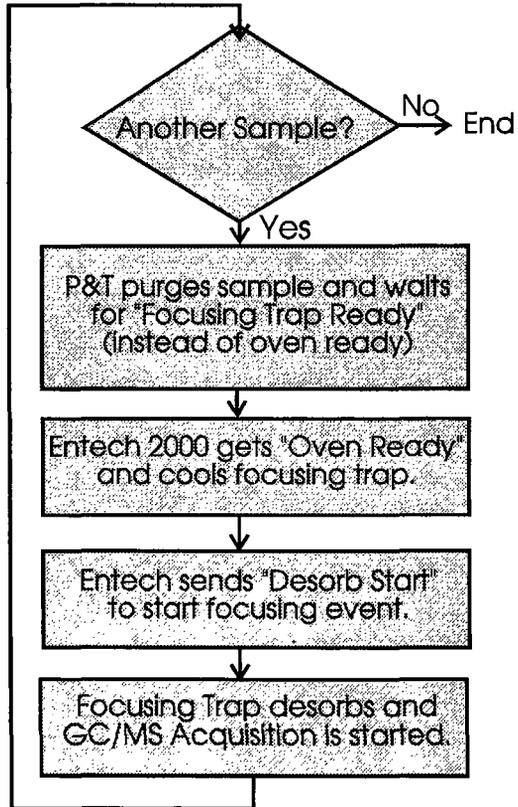
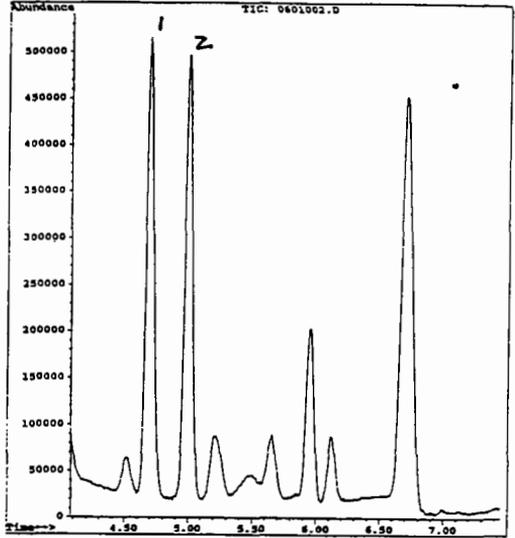


FIG 2

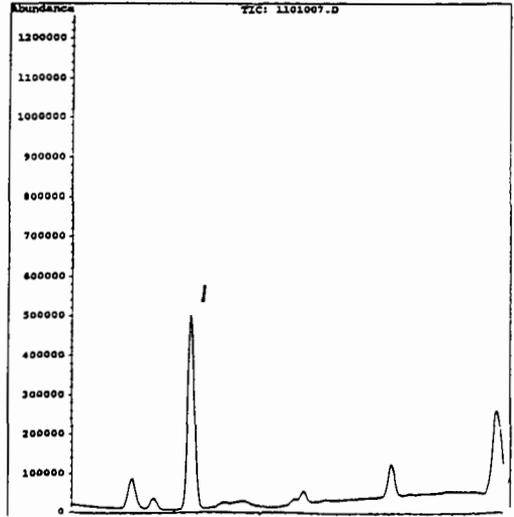
File : A:\0601002.D  
Operator : LL  
Acquired : 22 Apr 92 4:08 pm using AcqMethod v0420c1.M  
Instrument : MS 5971  
Sample Name : 9310202-003 MS 3.395G  
Misc Info :  
Vial Number: 6

FIGURE 3 - Soil sample spiked with a methanol solution containing chloromethane (1) and vinylchloride (2). Peak widths were comparable to those later in the analysis.



File : A:\1101007.D  
Operator : LL  
Acquired : 22 Apr 92 8:05 pm using AcqMethod v0420c1.M  
Instrument : MS 5971  
Sample Name : 9310202-001 1.297 G/100UL/SOUL  
Misc Info :  
Vial Number: 11

FIGURE 4 - Diesel contaminated soil sample containing a large abundance of vinylchloride (1).



## **AIR EMISSION RATE MEASUREMENTS OF SURFACE IMPOUNDMENT QUIESCENT WATER AND SLUDGE SURFACES**

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### **INTRODUCTION**

Two 17-acre surface impoundments located at a chemical manufacturing facility are required to be closed through an administrative consent order with a state environmental regulatory agency. The impoundments contain approximately 400,000 cubic yards of a 30 percent solids sludge. The sludge is contaminated with a variety of volatile and semivolatile organic compounds (VOCs collectively). Chlorobenzene and 1,2-dichlorobenzene are the predominant organic compounds present at average concentrations of 905 and 1,696 mg/kg (dry weight), respectively. A variety of heavy metals are also present in the sludge with lead being predominant at an average concentration of 12,716 mg/kg (dry weight).

Closure will consist of in-situ solidification followed by consolidation into a vault that will be constructed within the footprint of one of the impoundments. To facilitate the solidification process, the surface water will be completely removed from the impoundment. This could potentially result in a release of fugitive air emissions of VOCs from the sludge surface. State air quality regulations require control of these fugitive emissions if the emission rate of total VOCs exceed 0.5 lb/hr. To address the regulatory requirement, a study was developed to estimate the air emission rate of VOCs from the surface impoundment sludge surfaces, and determine how the air emission rate from the sludge surface varies with time after removing the surface water. The results were used to determine whether an emission control technology would be required to meet the regulatory requirement. The study also included estimating the emission rate of VOCs from the quiescent water surface for comparison purposes. This paper discusses the procedures, results, conclusions, and recommendations from the study.

### **PROCEDURES**

The air emission rate measurements were completed with the use of three emission isolation flux chambers (flux chambers). A flux chamber is an enclosure device which enables the user to make direct emission rate measurements of VOCs that are released from a defined water or land surface area. To measure the emission rate for this study, the flux chamber was placed over the desired location, and an ultra high purity air (<0.1 ppm total hydrocarbons) carrier gas was introduced into the flux chamber at a constant flow rate of 5 L/min. The carrier gas flow into the flux chamber enters at several points to facilitate complete mixing with the emissions from the defined surface area. The carrier gas flow creates a slight positive pressure within the flux chamber which prevents external air from entering the flux chamber and possibly contaminating or diluting the exhaust gas. However, the slight positive pressure is not enough to prevent the emissions from entering the flux chamber, because the pressure is continuously released through a 3/4-inch diameter vent on top of the flux chamber. The flux chamber design and operating procedures were obtained

from the *Measurement of Gaseous Emissions from Land Surfaces Using an Emission Isolation Flux Chamber - User's Guide* (EPA 600 8-86-008).

Samples were collected from the sample outlet, and analyzed for individual VOCs utilizing EPA Ambient Air Method TO-14. The Summa® canisters used for sample collection had regulators to limit the sample collection rate to 1 L/min. A portable organic vapor analyzer was utilized to monitor total organic vapor concentrations and evacuate the sample outlet prior to sample collection. Samples were collected after five residence times (30 minutes) to ensure that the carrier gas and emissions were completely mixed. With the analytical results, the emission rate of individual VOCs were then calculated from the following equation:

$$E_i = C_i Q / A$$

- $E_i$  = emission rate of component i ( $\mu\text{g}/\text{m}^2\text{-min}$ )  
 $C_i$  = concentration of component i in the sample ( $\mu\text{g}/\text{m}^3$ )  
 $Q$  = total gas flow rate (carrier gas and air emission) ( $5\text{E-}03 \text{ m}^3/\text{min}$ )  
 $A$  = surface area enclosed by the chamber ( $0.13 \text{ m}^2$ )

Emission rate measurements were conducted at three locations within the surface impoundment. A 10-ft long, 24-in diameter steel caisson was placed at each location to facilitate the measurements. Caissons A and B were located in areas containing average concentrations of VOCs, and Caisson C was located in an area known to contain higher concentration of VOCs. To complete the measurements at each location, the 1.5-foot of surface water was removed from within the caisson, and the flux chamber was installed in the caisson on top of the sludge surface. Figure 1 depicts the caisson with a flux chamber installed. Measurements of the sludge surface were completed initially and after 4, 8, 24, and 48 hours of exposure. A quiescent water surface measurement was also completed at each location by floating the flux chamber on the water with the use of a 16-inch inner tube.

## RESULTS

Table 1 presents the calculated emission rates in lb/sqft-hr of total VOCs for each caisson throughout the 48 hour time period. The results for each caisson are discussed in the following sections.

### Caisson A

For Caisson A, the emission rate of total VOCs ranged from  $5.20\text{E-}07$  lb/sqft-hr initially to  $1.63\text{E-}07$  lb/sqft-hr at 48 hours. The lowest emission rate of total VOCs was  $1.49\text{E-}07$  lb/sqft-hr which occurred at 8 hours. Initially, Freon® 113 was emitted at the highest rate of  $3.49\text{E-}07$  lb/sqft-hr (67.1 percent of the total). FREON is not defined as a VOC by the state's regulations due to its non-photoreactive properties. However, it is included in the total VOC emission rates discussed in this paper since it appears to be the predominant compound emitted from the sludge surface. FREON was not analyzed for in sludge sample analyses, because it was not included as on the standard list of analytes. Toluene and chlorobenzene were emitted at the next highest rates of  $6.42\text{E-}08$  and  $5.23\text{E-}08$  lb/sqft-hr, respectively. At 48 hours, FREON 113 was emitted at the highest rate of  $1.12\text{E-}07$  lb/sqft-hr (68.7 percent of the total). 1,2,4-trichlorobenzene and 1,2-dichlorobenzene were emitted at the next highest rates of  $2.49\text{E-}08$  and  $7.11\text{E-}09$  lb/sqft-hr, respectively. No significant changes in the emission rate were observed after 8 hours of exposure.

## Caisson B

For Caisson B, the emission rate of total VOCs ranged from 7.12E-07 lb/sqft-hr initially to 1.02E-07 lb/sqft-hr at 48 hours. The lowest emission rate of total VOCs was 6.25E-08 lb/sqft-hr which occurred at 24 hours. Initially, FREON 113 was emitted at the highest rate of 6.84E-07 lb/sqft-hr (96.1 percent of the total). Chlorobenzene and FREON 114 were emitted at the next highest rates of 9.58E-09 and 6.50E-09 lb/sqft-hr, respectively. At 48 hours, FREON 113 was emitted at the highest rate of 9.00E-08 lb/sqft-hr (88.2 percent of the total). FREON 114 and chlorobenzene were emitted at the next highest rates of 3.10E-09 and 2.72E-09 lb/sqft-hr, respectively. No significant changes in the emission rate were observed after 8 hours of exposure.

## Caisson C

Caisson C had the highest emission rate of total VOCs compared to the other caissons. This was expected since the sludge in that area of the surface impoundment contains higher concentrations of VOCs. The emission rate of total VOCs ranged from 2.36E-06 lb/sqft-hr initially to 4.94E-07 lb/sqft-hr at 48 hours. The lowest emission rate of total VOCs was 4.53E-07 lb/sqft-hr which occurred at 24 hours. Initially, 1,2,4-trichlorobenzene was emitted at the highest rate of 8.78E-07 lb/sqft-hr (37.2 percent of the total). Freon® 113 and 1,2-dichlorobenzene were emitted at the next highest rates of 6.84E-07 and 6.26E-07 lb/sqft-hr, respectively. At 48 hours, 1,2,4-trichlorobenzene was emitted at the highest rate of 2.35E-07 lb/sqft-hr (47.6 percent of the total). 1,2-dichlorobenzene and FREON 113 were emitted at the next highest rates of 1.34E-07 and 8.28E-08 lb/sqft-hr, respectively. No significant changes in the emission rate were observed after 8 hours of exposure.

## Quiescent Water Surface

Table 1 also presents the calculated emission rates in lbs/sqft-hr of total VOCs from the quiescent water surface adjacent to Caissons B and C. Data is not available for the quiescent water surface adjacent to Caisson A due to the SUMMA canister leaking during transport to the laboratory. The total VOC emission rate for Caisson B was 1.20E-07 lb/sqft-hr with FREON 113 being emitted at the highest rate of 8.64E-08 lb/sqft-hr (72.0 percent of the total). 1,2-dichlorobenzene and chlorobenzene were the only other compounds emitted at rates of 2.02E-08 and 1.35E-08 lb/sqft-hr, respectively. The total VOC emission rate for Caisson C was 5.09E-08 lb/sqft-hr with FREON 113 being emitted at the highest rate of 1.98E-08 lb/sqft-hr (38.9 percent of the total). 1,2-dichlorobenzene and chlorobenzene were emitted at the next highest rates of 1.93E-08 and 9.15E-09 lb/sqft-hr, respectively.

## Overall Air Emission Rate

Table 1 also presents the overall total VOC emission rate from the impoundment. This was calculated by multiplying the average total VOC emission rate of all the caissons combined by the surface area of the surface impoundment (17.4 acres = 757,944 sqft). The air emission rate ranges from 0.91 lb/hr initially to 0.19 lb/hr at 48 hours. At 4 hours, there is a 69.2 percent reduction of the total VOC emission rate. At 8 hours, there is a 76.9 percent reduction. No significant changes in the emission rates occur after 8 hours of exposure. The quiescent surface emission rate is 0.06 lb/hr, which indicates that the surface water is effectively suppressing the emission rate of VOCs from the sludge surface. Figure 2 is a graphical representation of the overall emission rate of total VOCs versus time.

## CONCLUSIONS

The following conclusions can be drawn from the results of this study:

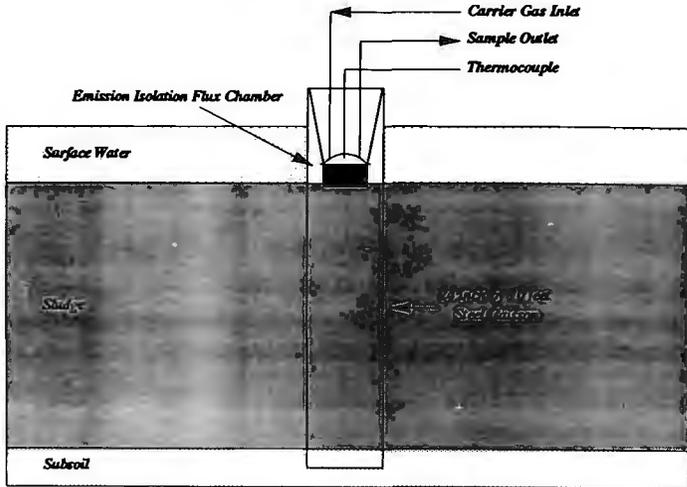
- The emission rate of total VOCs from Caisson C was higher than the emission rates from the other caissons. This was expected since the sludge in the area of Caisson C contains higher concentrations of VOCs.
- The quiescent water surface emission rates are less than the lowest sludge surface emission rates, which indicates that the surface water does effectively suppress the emission rate of total VOCs from the sludge surface.
- A 69.2 percent reduction of total VOC emissions occurs at 4 hours, and this corresponds to 87.5 percent of the total reduction from the initial to the 48 hour measurement.
- No significant change in total VOC emission rates occurs after 8 hours of exposure.
- FREON 113 is the predominant compound emitted from the sludge surface, but is not defined as a VOC by the state regulations due to its non-photoreactive properties.
- The initial and highest emission rate of total VOCs including FREON 113 from the sludge surface is 0.91 lb/hr.
- Based on these results of this study, emissions control will not be required during or following the removal of surface water from the impoundment, because the maximum emission rate of total VOCs excluding FREON 113 does not exceed the state's regulatory requirement of 0.5 lb/hr.

## RECOMMENDATIONS

The following recommendations are made based on the results of this study:

- A dispersion model should be completed with this data to determine what the concentrations of VOCs will be at the site boundaries, and whether these concentrations will affect human health and/or cause odor problems.
- It is recommended that the impoundment be drained slowly in order to minimize the amount of surface area being exposed at one time; therefore, reducing the overall initial emission rates from the sludge surface. Table 2 presents the overall air emission rate of total VOCs from the sludge surface after the water level is decreased a 0.5 foot per day until no more water is present. The table shows that even with FREON 113 included, the overall emission rate of total VOCs would be less than the state's regulatory requirement of 0.5 lb/hr.

**FIGURE 1**  
**Field Apparatus Setup**



**TABLE 1**  
**Calculated Air Emission Rates for Total VOCs**

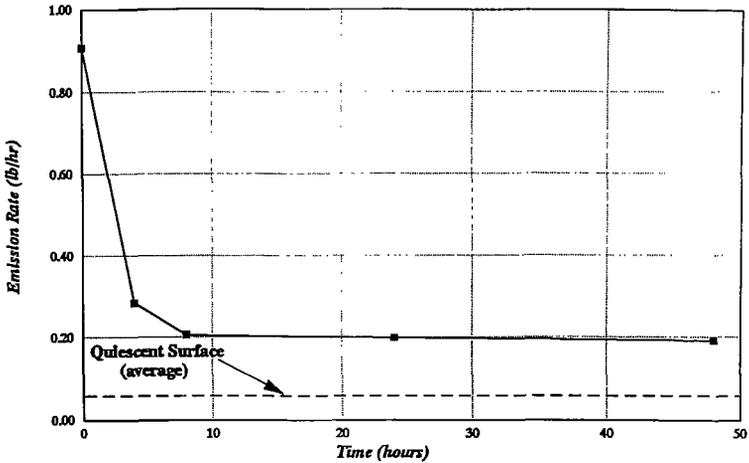
Measurement	Caisson A Total VOC (lb/sqft-hour)	Caisson B Total VOC (lb/sqft-hour)	Caisson C Total VOC (lb/sqft-hour)	Average Total VOC (lb/sqft-hour)	Overall Emission Rate (lb/hr)
Quiescent Surface	NA	1.20E-07	5.09E-08	8.55E-08	0.06
Initial	5.20E-07	7.12E-07	2.36E-06	1.20E-06	0.91
4 Hours	2.95E-07	1.45E-07	6.83E-07	3.74E-07	0.28
8 Hours	1.49E-07	1.02E-07	5.64E-07	2.72E-07	0.21
24 Hours	2.44E-07	6.25E-08	4.80E-07	2.62E-07	0.20
48 Hours	1.63E-07	1.02E-07	4.94E-07	2.53E-07	0.19

**Notes:**

(1) - NA (not analyzed).

(2) - The overall emission rate is calculated by multiplying the average emission rate by the surface impoundment's surface area of 757,944 sqft.

**FIGURE 2**  
**Overall Total VOC Air Emission Rate versus Time**



**TABLE 2**  
**Air Emission Rates of Total VOCs**  
**Resulting from Removing the Surface Water**

Water Level (feet)	Quiescent Surface Total VOC (lb/hr)	New Sludge Surface Total VOC (lb/hr)	Sludge Surface Total VOC (lb/hr)	Overall Total VOC (lb/hr)
4.50	0.06 (757,944 sqft)	0.00 (0 sqft)	0.00 (0 sqft)	0.06
4.00	0.05 (629,778 sqft)	0.15 (128,166 sqft)	0.00 (0 sqft)	0.20
3.50	0.04 (488,498 sqft)	0.16 (141,280 sqft)	0.03 (128,166 sqft)	0.23
3.00	0.03 (303,123 sqft)	0.22 (185,375 sqft)	0.07 (269,446 sqft)	0.32
2.50	0.01 (157,376 sqft)	0.17 (145,747 sqft)	0.12 (454,821 sqft)	0.30
2.00	0.01 (78,001 sqft)	0.10 (79,375 sqft)	0.15 (600,568 sqft)	0.26
1.50	0.00 (0 sqft)	0.09 (78,001 sqft)	0.18 (679,942 sqft)	0.27
1.5 (after 24 hours)	0.00 (0 sqft)	0.00 (0 sqft)	0.20 (757,944 sqft)	0.20

**Notes:**

- (1) -  $8.55E-08$  lb/sqft-hr was the emission rate used for the quiescent surface (average quiescent surface emission rate).
- (2) -  $1.20E-06$  lb/sqft-hr was the emission rate used for the new sludge surface (average initial emission rate).
- (3) -  $2.58E-07$  lb/sqft-hr was the emission rate used for the sludge surface (average of the 24 and 48 hour average emission rate).
- (4) - The surface area for each specific surface is located below the corresponding emission rate.

## Characterization of Air Emissions From the Simulated Open Combustion of Fiberglass Materials

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### ABSTRACT

The exposure of persons to fiberglass combustion emissions in structure fires, fires at waste landfills, and fires at demolition sites has become an issue of increasing concern. This study identifies and quantitates a broad range of pollutants that are discharged during the small-scale, simulated, open combustion of fiberglass and reports these emissions per mass of fiberglass material combusted. Two types of fiberglass materials (representing the boating and building materials industries) were combusted in a controlled outbuilding designed for the simulation of open burning processes. Volatile, semivolatile, and particulate-bound organics were collected and analyzed by gas chromatography/mass spectrometry (GC/MS). The emphasis of these analyses was on the quantification of hazardous air pollutants listed in Title III of the Clean Air Act Amendments of 1990 (CAAAAs), although further efforts were made to identify and quantify other major organic components. Additional sampling and analysis were done for particulate-phase metals, respirable fibers, and hydrogen chloride. Fixed combustion gases (carbon dioxide, carbon monoxide, nitrogen oxide, oxygen and total hydrocarbons) were monitored continuously throughout the test period. Analytical results show substantial emissions of a large number of pollutants including carbon monoxide, particulate, lead, arsenic, benzene, toluene, styrene, naphthalene, phenol, dibenzofuran, phenanthrene, and benzo(a)pyrene.

### INTRODUCTION

Concerns over exposure to air emissions from the open burning of fiberglass in structure fires, and at waste disposal and demolition sites have been expressed to the Control Technology Center (CTC) of the U.S. Environmental Protection Agency (EPA). Though little previous research has been done specifically on combustion emissions from fiberglass, literature does exist relating to the composition of fiberglass, the combustion products of some components of commercial fiberglass materials, and the suspected health effects of fiberglass fibers. Fiberglass is principally composed of  $\text{SiO}_2$  (approximately 50% by weight); additional major components are  $\text{Al}_2\text{O}_3$ ,  $\text{Ba}_2\text{O}_3$ ,  $\text{CaO}$ , and  $\text{MgO}$  (typically 3 to 20% each) and trace components include F,  $\text{Fe}_2\text{O}_3$ ,  $\text{K}_2\text{O}$ ,  $\text{Na}_2\text{O}$ ,  $\text{SO}_3$  and  $\text{TiO}_2$  (less than 1% by weight each<sup>1</sup>). Additionally, fiberglass materials may contain organics as sizings or binders.<sup>1</sup> Organic containing fiberglass materials can be classified as either epoxy based or polyester based.<sup>2</sup> The known combustion products of polyester-based materials have been reviewed and are known to include acetaldehyde, benzene, biphenyl, carbon monoxide, ethyl benzene, pentadiene, styrene, and toluene.<sup>3-6</sup> Much of the available information on these combustion products has been obtained in small-scale studies of materials that are likely to be less complex than the commercial materials found in practice. Therefore, larger scale tests of complex commercial materials promise increased insight.

In addition to potential hazards of a chemical nature, the air emissions from open fiberglass combustion may include fibrous aerosols; the physical nature of fibrous aerosols may lead to additional health hazards. Epidemiological studies have shown significant increases in non-malignant respiratory disease in populations exposed to glass fibers.<sup>7</sup> Glass fibers are apparently less harmful to health than asbestos fibers.<sup>8</sup> The greatest hazard appears to be related to fibers with a diameter less than  $1.5 \mu\text{m}$  and a length greater than  $8 \mu\text{m}$ .<sup>8</sup> No measurements of fiberglass fiber emissions from combustion processes have been found in our literature review to date. An assessment of the concentration and size distribution of fibrous aerosols produced from fiberglass open combustion processes would be valuable.

In response, through the guidance of EPA's Air and Energy Engineering Research Laboratory (AEERL), a study was undertaken to measure emissions from the combustion of fiberglass samples from two industries that use fiberglass extensively. This study included replicate tests of fiberglass materials from the boating industry (polyester based, some with and some without a gel coating (an epoxy based sealing material)), and the building industry (vinylester based). The study was designed to collect, identify, and quantify a wide range of air emissions and to report these emissions per mass

of fiberglass material combusted. The emphasis of these analyses was on the quantification of air toxics compounds listed in the Clean Air Act Amendments of 1990 (CAAAAs), although further efforts were made to identify and semiquantify other major organic components. Because of the complexity of this study, this paper can only highlight the methods used and the results obtained. The reader is urged to consult the forthcoming EPA report on this project for more complete information.

## METHODS

Combustion testing for this study occurred in EPA's Open Burning Simulation facility, which has been previously described.<sup>9</sup> The boating industry fiberglass samples were placed in the facility and ignited using a brief application of a handheld propane torch which was removed before sampling began. A "hut blank" test in which the propane torch was briefly introduced into the facility but no fiberglass was combusted was conducted for comparison purposes. In order to allow an adequate time period for all necessary samples to be obtained, three separate charges of fiberglass were combusted during each test. Combustion of one charge was allowed to go to apparent completion (as signified by constant weight and near background concentrations of combustion gases) before another charge was introduced. Attempts to test the building industry fiberglass sample in a like manner were unsuccessful because of the high concentration of flame retardant in this sample. Therefore, the combustion of the building industry material was supported by a continuous liquid propane (LP) gas flame during sampling. This study design was intended to simulate the behavior of this flame retarded fiberglass material in the presence of other non-flame retarded combustibles. A "combustion blank" test in which the LP flame was operated but no fiberglass was present was conducted for comparison purposes. In addition, various field and laboratory blank samples were collected for each sampling train, as appropriate. In order to allow an adequate time period for all necessary samples to be obtained, two separate charges of fiberglass were combusted during each test. Combustion of one charge was allowed to go to apparent completion, as was done for the boating industry samples before another charge was introduced.

An elemental analysis of the fiberglass samples was performed before combustion using methodologies best summarized by ASTM methods 3176 and 3172.<sup>10</sup> Fixed combustion gases [carbon dioxide (CO<sub>2</sub>), carbon monoxide (CO), nitric oxide (NO), oxygen (O<sub>2</sub>), and total hydrocarbons (THC)] were monitored continuously throughout the test period through the sampling manifold. Temperatures at relevant locations in and around the test facility and the mass of fiberglass material were monitored throughout the test period.

Volatile organics were collected from the sample manifold on sorbent tubes (VOST train) and analyzed by gas chromatography/mass spectrometry (GC/MS).<sup>11,12</sup> Since extremely high levels of volatile organic compounds were observed during early tests of the building industry fiberglass, an additional volatile sampling method was implemented. Samples were collected in Tedlar<sup>®</sup> bags and analyzed by GC/MS in accordance with EPA Method 18.<sup>13</sup> Samples for semivolatile and particulate-bound organics and metal aerosol analysis were collected through separate medium volume PM<sub>10</sub> samplers located in the burn hut.<sup>14</sup> The sample for metal aerosol was collected on a 142 mm diameter quartz fiber filter and analyzed by inductively coupled plasma-atomic emission spectrometry in accordance with an EPA contract laboratory program method (similar to EPA method 200.7<sup>15</sup>). The semivolatile and particulate phase organic sample was collected with a 142 mm diameter, Teflon impregnated, glass fiber filter and XAD-2 resin sorbent. The filter and resin were then extracted in methylene chloride, and the pooled extract was analyzed in accordance with EPA Method 8270.<sup>16</sup> A realtime photoelectric analyzer designed to quantify total polycyclic aromatic hydrocarbons (PAHs) on submicron particulate was also operated using a sample stream withdrawn through the sampling manifold.<sup>17,18</sup> A sample probe for vapor-phase hydrogen chloride was also located in the burn hut. These samples were analyzed by ion chromatography. This sampling was done according to a modified form of EPA Method 26.<sup>13</sup>

The sampling train used to sample for fiber size and morphology analysis consisted of a 37-mm mixed cellulose ester filter cassette followed by a low volume sampling pump and dry gas meter. The filter was operated in an inverted position, parallel to the facility floor during sampling to minimize the collection of particulate matter through gravitational settling. Analysis was performed by phase contrast light microscopy (PCM) and transmission electron microscopy (TEM). For the purposes of these analyses, a fiber was defined as a particle with an aspect ratio of greater than 3:1. These sampling and analysis methodologies were based on NIOSH methods for asbestos fibers.<sup>19</sup>

After the completion of the chemical and microscopic analyses, analyte concentration data were coupled with sample volume, facility air flow, and combustible material mass loss data to derive estimated emissions (expressed as mass of analyte produced per mass of fiberglass material consumed in the combustion process).

## RESULTS AND DISCUSSION

The elemental analysis of the fiberglass materials before combustion (Table 1) indicates that the organic matter content of the boating industry fiberglass is higher than the building industry material. The substantial halogen concentration found in the building industry material tends to confirm the manufacturer's statement that the material contained a brominated fire retardant. The vast majority of the combustion of each charge of boating industry material was completed in a 20-40 minute time period while the majority of the building industry material in each charge appeared

to be consumed in 30-60 minutes. Table 2 summarizes the estimated emissions derived from realtime measurements of CO, CO<sub>2</sub>, THC, and total PAH bound to submicron particulate. The substantial observed CO emissions, which are probably underestimated in this data set, are a concern since CO is believed to be the "primary cause of death of most fire victims."<sup>4</sup> Substantial emissions of particulate matter were also observed (average values were 117 g/kg for the boating industry material and 607 g/kg for the building industry material). This is a concern since a majority of previous studies of combustion products of various polymers have paid little attention to the composition of the particulate phase.<sup>5</sup>

The volatile organic data set includes concentration measurements for 35 targeted (the majority of which are consistently non-detectable) and several dozen tentatively identified species; Table 3 presents average data on several selected compounds that were among those seen in the highest levels. It appears that the relative ratios of these components are similar for both the boating and building industry materials but that the absolute emission rate is higher for the building industry material.

Table 1. Composition of Fiberglass Materials Tested (all data as % composition).

	Boating Industry Fiberglass - Without Gel Coat	Boating Industry Fiberglass - With Gel Coat	Building Industry Fiberglass
Carbon	52.97	55.06	25.33
Hydrogen	4.79	5.27	2.48
Oxygen	7.1	<0.5	10.06
Nitrogen	0.017	0.015	<0.5
Sulfur	<0.03	<0.03	<0.5
Total Halogen (as Cl)	<0.5	<0.5	1.9
Aluminum	0.28	0.081	2.2
Magnesium	<0.05	<0.05	0.12
Cadmium	<0.004	<0.004	<0.01
Chromium	0.0091	0.041	0.086
Moisture	2.06	1.19	0.52
Volatile Matter	63.11	56.24	35.29
Ash	34.83	39.57	60.23
Fixed Carbon	<0.1	3	3.96

Table 2. Combustion Gas and PAH Particulate Analyzer Concentrations and Estimated Emissions

Date	Test	CO as C Estimated Emissions (g/kg)*	CO <sub>2</sub> as C Estimated Emissions (g/kg)*	THC as Methane Estimated Emissions (g/kg)*	PAH Estimated Emissions (g/kg)
09/08/92	First Boating Industry Test	48.2	980.8	41.6	1.48
09/17/92	Second Boating Industry Test	55.2	953.4	40.5	0.85
10/13/92	First Building Industry Test	205.9	NC	270.3	0.97
10/30/92	Second Building Industry Test	141.4	NC	202.3	0.58
11/04/92	Third Building Industry Test	163.3	NC	232.2	0.59

Key: NC = Not calculated (estimated emissions were not calculated for CO<sub>2</sub> in the building industry test since the LP burner contributed a sizeable and somewhat variable percentage of the emissions).  
 \* = In cases where some measured concentrations exceeded the concentration of the high calibration point before calculating the averages, the data were truncated to the high calibration point.

Table 3. Estimated Emissions of Selected Volatiles

Compound	Boating Industry VOST Samples, Average Estimated Emissions (g/kg)	Building Industry Tedlar Bag Samples, Average Estimated Emissions (g/kg)
Benzene	5.9	34.8
Ethyl Benzene	0.7	9.3
Styrene	4.5	49.4
Toluene	3.6	18.0
m-p-Xylene	0.5	1.1

The semivolatile and particulate bound organics data set generated from this project includes concentration measurements for more than 90 targeted (the majority of which were consistently non-detectable) and several dozen tentatively identified species. Average emission values for a selected set of detected, targeted semivolatile, and particulate bound organics are presented in Table 4. Average estimated emissions for these compounds are generally lower than for the volatile species discussed previously. As in previous measurements, the values obtained in the building industry fiberglass tests are generally higher than those in the boating industry tests. Preliminary calculations have shown that the estimated emissions calculated from the output of the real time PAH analyzer (Table 2) agree at least within a factor of 10 with the sum of estimated emissions calculated from the Method 8270 analyses of PAHs that would be expected to be predominantly in the particulate phase.

Table 4. Estimated Emissions of Selected Semivolatiles

Compound	Boating Industry Average (mg/kg)	Building Industry Average (mg/kg)
Anthracene	353	202
Benzo(a)pyrene	86	72
Biphenyl	689	1,936
Chrysene	323	458
2-Methyl Phenol	125	400
Phenanthrene	902	2,156
Phenol	328	6,830

Fibrous aerosols samples rarely showed significantly more fibers than were seen in blank samples, as shown in Table 5. However, detection limits were quite high for this analysis, since the maximum feasible loading of total particulate on these filters was reached after a very small volume (<20 L) was sampled and it is only feasible to conduct the microscopic examination on a small representative portion of the filter surface area.

Table 5. Fibrous Aerosol Measurements

Sample No.	Test Date	Test	PCM Length >5 um Estimated Emissions (million S/kg)	ATEM Length >0.5 <5.0 um Estimated Emissions (million S/kg)	ATEM Length >5 um Estimated Emissions (million S/kg)
7	09/17/92	Second Boating Industry	1710	490*#	420*#
8	09/17/92	Second Boating Industry	4846*	1902*#	1902*#
11	09/17/92	Second Boating Industry	504*	NFD*#	NFD*#
16	10/13/92	First Building Industry	1904*	395*	395*
17	10/13/92	First Building Industry	432*	89*#	89*#
19	10/30/92	Second Building Industry	231*#	120*#	120*#

Key: NFD = No fibers detected, detection limit cannot be stated accurately due to loading problems  
 PCM = Phase contrast microscopy  
 ATEM = Analytical transmission electron microscopy  
 \* = Number of observed fibers not greater than 3 times larger of the applicable field and hut blank values  
 # = Air concentration of observed fibers not more than 3 times larger than the applicable hut or combustion blank value  
 S = Fibrous Structures

The particulate-phase metals samples were analyzed for 11 elements. Of these, only lead, silver, and possibly cadmium were detected in the boating industry emissions and only arsenic and possibly chromium were detected in the building industry emissions. These results are summarized in Table 6.

Table 6. Metals Estimated Emissions (mg/kg)

Test	Silver	Arsenic	Cadmium	Chromium	Lead
First Boating Industry	4.41	0.52*#	0.06*#	1.57*#	21.00
Second Boating Industry	4.60	0.6*#	0.29	0.48*#	38.72
Boating Industry Average	4.50	0.56	0.18	1.03	29.86
First Building Industry	13.38*	6.13*	0.28*#	8.92	2.79*#
Second Building Industry	14.45*	48.15	0.80*	14.45*	8.03*
Third Building Industry	6.76*#	13.05	0.24*#	5.80*#	2.42*#
Building Industry Average	11.53	22.44	0.44	9.72	4.41

Key: \* = Mass of this sample not greater than 3 times the largest of the following: mass in field blank, mass in hut blank, or mass in combustion blank, as applicable.  
 # = Sample hut air concentration not greater than 3 times the hut blank air concentration or the combustion blank air concentration, as applicable.

Vapor-phase hydrochloric acid was not detected in any of the samples analyzed. Detection limits varied from 40 to 260 mg/kg. No other acid gases were analyzed for.

Because of operational difficulties (i.e., sampling media overloading), the sampling periods for various trains varied widely. Thus, it is not possible to compute an accurate mass balance on this system since the rates of emission of various pollutants probably vary during various phases of the combustion process. In addition, since the rate of emissions from a small mass of combusted fiberglass was high enough to threaten overloading of the sampling media, it was necessary to sharply limit the amount of fiberglass combusted in each test phase. This may introduce a significant source of error into the data set because the resolution of the balance used to measure the weight of fiberglass lost to combustion was 0.2 lb (0.09 kg), (the average weight losses for the samples were: organic semivolatiles/particulate train 3.0 lb (1.4 kg), metals train 3.8 lb (1.7 kg), VOST train 0.9 lb (0.4 kg), Tedlar® bag train 2.0 lb (0.91 kg), CEM train 8.3 lb (3.8 kg), fiber train 1 lb (0.45 kg), hydrochloric acid train 7.2 lb (3.3 kg)).

## CONCLUSION

Despite the aforementioned experimental difficulties, this project did succeed in producing estimated emissions data for a broad range of atmospheric pollutants from a simulated open fiberglass combustion process. Substantial emissions of a large number of pollutants including carbon monoxide, particulate, lead, arsenic, benzene, toluene, styrene, naphthalene, phenol, dibenzofuran, phenanthrene, and benzo(a)pyrene were observed. The health implications of these emissions in a given situation can be judged if emissions data such as those presented here are combined with fate and transport, and health effects data to form a detailed risk assessment.

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**INITIAL IMPLEMENTATION OF THE PHOTOCHEMICAL ASSESSMENT  
MONITORING STATIONS (PAMS) NETWORK**

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**ABSTRACT**

Section 182(c)(1) of the 1990 Clean Air Act Amendments requires the Administrator to promulgate rules for the enhanced monitoring of ozone, oxides of nitrogen, and volatile organic compounds to obtain more comprehensive and representative data on ozone pollution. Following promulgation on February 12, 1993, states with ozone nonattainment areas classified as serious, severe, and extreme must adopt and implement a program to monitor for such pollutants.

The PAMS network is driven by new monitoring requirements for VOCs, carbonyls, and meteorological measurements. For the first time, State and local agencies will be required to report data quarterly to the U.S. EPA for non-criteria pollutants. There are no reference or equivalent methods available to measure VOCs nor are there National Ambient Air Quality Standards (NAAQS) for these pollutants. Agencies will be learning to operate sampling equipment that is often state-of-the-art and currently undergoing development. Routine sampling for these pollutants has never been attempted on this scale and will therefore make implementation of this network challenging, at the least.

## **INTRODUCTION**

On February 12, 1993, the Environmental Protection Agency published amendments to the ambient air quality surveillance rules (40 CFR 58) to provide for the enhanced monitoring of ozone and oxides of nitrogen and for the additional monitoring of volatile organic compounds (including carbonyls)(58 FR 8452). Affected agencies must submit a State Implementation Plan revision to provide for the establishment and maintenance of a PAMS network within 9 months after this date or 9 months after the date of redesignation or reclassification of any existing ozone nonattainment area or the designation of a new area to serious, severe, or extreme. Even more stringently, these areas must submit a PAMS network description, including a schedule for implementation within 6 months of the above mentioned criteria. The first site should be initiated by February of 1994 (within a year of promulgation), and fully operational by June of 1994.

## **AFFECTED AGENCIES**

There are twenty-two ozone non-attainment areas in the country that have been designated as serious, severe, or extreme, and are currently affected by this regulation. The State and local Air Pollution Control Agencies in these areas are responsible for implementing this regulation by establishing specialized ambient air monitoring stations. These stations will monitor for ozone, oxides of nitrogen, meteorology, and most importantly for volatile organic compounds (VOCs) and carbonyls. The reason that VOCs are so important is that never before have agencies been required to report to the EPA not only VOCs, but speciated VOCs as well.

Now, let's consider this from the perspective of a State or local agency. If EPA were to tell them that they had to monitor for something totally new, something for which there are no reference or equivalent methods with which to obtain these measurements, something for which there is no National Ambient Air Quality Standard (NAAQS), something that has never been measured routinely, is barely out of the research phase, and they presently don't even have enough staff to do the job at hand for the criteria pollutants, their reaction would probably be less than enthusiastic.

EPA's response would then be to remind them that this is not to be taken lightly and is required by the regulation. This might cause anger and opposition until EPA advises them that due to the magnitude of the program, they are willing to assist in the following ways: 1) Funding in the way of grant dollars. EPA would provide 105 Grant Funds in proportion to the number of sites required in each Region. The Regions would then disperse this money to the affected agencies. 2) Training in the way of workshops. EPA has already conducted the National PAMS Teleconference Workshop which was broadcasted to over 200 downlink sites across the nation. Topics ranged from Program Requirements and Implementation to Sampling and Analysis to Data Uses and Quality Assurance.

3) Technical support in the way of guidance and calibration and audit materials. A Technical Assistance Document for the Sampling and Analysis of Ozone Precursors has been distributed, as well as Guidance on the Development and Approval of PAMS Network Plans, PAMS Program and Data Quality Objectives, and Network Design and Siting. Calibration and retention time standards for VOCs will be supplied from a centralized source, and proficiency samples will be disbursed routinely for quality assurance purposes.

## **IMPLEMENTATION CONCERNS**

Once the decision has been reached to proceed with implementation, a variety of concerns, questions, and problems arise. The following concerns were addressed at the PAMS Teleconference Workshop on April 27-30, 1993, which was sponsored by the Office of Air Quality Planning and Standards and the Atmospheric Research and Exposure Assessment Laboratory (AREAL).

1. When does the network need to be implemented ?

The network design plan is due in August 1993, and the first site needs to be fully operational in June 1994. However, the program was funded a year in advance by EPA 105 grant money so that the first sites could be operational in June 1993, and in fact are encouraged to be. Almost all of the 22 affected areas will be performing sampling, although some on a reduced frequency, this summer.

2. Has anyone out there done this before ?

There have been numerous research studies conducted in the past few years by AREAL, the Lake Michigan Air Directors Consortium (LADCO), and the California Air Resources Board (CARB), to name a few. Approximately half of the affected areas were doing PAMS sampling for VOCs on a reduced frequency during the 1992 Air Toxics Initiative, which was a program funded to establish volatile organic compound/toxics and aldehyde monitoring sites in a select number of urban areas in 1992. The establishment of these sites allowed the early implementation of baseline monitoring to support the PAMS program by collecting background data on VOC and aldehyde concentrations in the atmosphere before gasoline reformulation and other control programs take effect. They were later to be supplemented with instruments to sample for pesticides, PAHs,

**PCBs, and metals.**

**3. How are samples for VOCs collected ?**

Manual methods utilize canisters. Automated methods utilize the continuous automated gas chromatographs. The automated methods presently available differ in their abilities to cool the column ovens by the use of liquid nitrogen or liquid carbon dioxide or the use of thermoelectric coolers.

**4. How are samples for VOCs analyzed ?**

Both methods utilize a gas chromatograph with a flame ionization detector.

**5. What kind of instrumentation is available for automated systems ?**

The following vendors have demonstrated that their instruments are capable of sampling and analyzing according to the guidelines referenced in the regulation (58 FR 8452):

Perkin-Elmer Corporation  
Graseby-Nutech Corporation  
Chrompack  
Varian Chromatography Systems  
Entech Laboratory Automation

**6. How is the data going to be used ?**

The data can be used in the following ways: 1) As evaluation tools for control strategies, cost effectiveness, and for understanding the mechanisms of pollutant transport. 2) As a baseline for model evaluation and to minimize model adjustments and reliance on default settings. 3) In analyzing emissions inventory issues and corroborating progress toward attainment. 4) In the preparation of unadjusted and adjusted pollutant trends reports. 5) To make attainment/nonattainment decisions and to construct NAAQS maintenance plans. 6) To evaluate population exposure to air toxics as well as criteria pollutants.

**7. How is the data going to be quality assured ?**

AREAL will be supplying calibration and retention time standards from a centralized source for consistency and comparability of the data nationwide. The agencies will be paying for these with their grant dollars. AREAL will also be

providing materials with which to perform proficiency studies. Since some programs are overlapping across States and EPA Regions, these areas will be conducting programs to include oversight, quality assurance plans, site visits, and audits to provide for consistency and comparability from agency to agency.

**8. What if an agency wants to do something different ?**

The regulation does provide for the submittal of alternative plans in the areas of siting (number and arrangement), methodology (sampling and analysis), monitoring season (months with highest ozone), sampling frequency, and meteorology (establishing wind directions for siting).

Once some of these initial concerns are addressed, an agency should get started by submitting their procurement requests for instrumentation and then by deciding where to locate their monitors. The information gathered to make these decisions must be packaged and submitted to EPA for network approval. This is due to the requirements of the regulation (58 FR 8452). The requirements for this network are the same as for the NAMS network and therefore must be approved in the same way, by the Technical Support Division Director. The plan is sent from the States to the Regional Office who sends it to OAQPS. The PAMS network review committee consisting of the core committee, a meteorologist, a modeler, an emissions expert, and an AREAL representative, in conjunction with the Regional Office involved will reach a consensus on the plan and then send their recommendations on to management for final approval.

## **CONCLUSION**

EPA is currently reviewing plans for the first site location. This location is to be representative of the maximum precursor emissions of the non-attainment MSA. Most agencies have already submitted their plans, however a few are still in the developmental stages. If all goes well, we expect to have some data reported to the Aerometric Information Retrieval System by January 1994 from the sites that are operational in June of 1993. During each year of implementation, as another site is added and data are analyzed from sites already in operation, many of the problems, concerns, and obstacles dealing with the start of a new monitoring network will be alleviated. The lessons learned in the initial stages of start-up, although painful, will prove to be invaluable as the implementation of the network continues.

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## Meteorological Considerations in Siting Monitors of Photochemical Pollutants

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### ABSTRACT

Ozone conducive meteorological conditions are identified based on statistics derived from local meteorological data of 31 eastern US cities in a 10-year (1981-1990) period. A method of using ozone conducive meteorological conditions to construct a windrose to site photochemical pollutant monitors is presented. The derived ozone conducive criteria appear to be quite robust, suggesting that the method may be applicable to site photochemical pollutant monitors in other areas of the United States.

### INTRODUCTION

Ozone is not directly emitted into the atmosphere but is formed photochemically from two major primary pollutants, volatile organic compounds (VOC) and nitrogen oxides (NO<sub>x</sub>). The accumulation of photochemically produced ozone, however, depends heavily on the dispersion and transport of pollutants by the wind field. Thus, ambient ozone concentrations can reach high levels only when the meteorological conditions are conducive both photochemically and dispersively. For this reason, meteorological conditions observed on high ozone days are often different from those observed on low ozone days. The ozone conducive meteorological conditions are high insolation, high temperature, high stability, low winds and low relative humidity. These ozone conducive conditions can only exist in special weather systems, such as stagnant high pressure system and quasi-stationary front or trough<sup>1,2</sup>. Therefore, applying the conventional method of using the (yearly or seasonally averaged) predominant wind direction(s) (PWD) as the sole guide for siting ozone and its precursors monitors<sup>3</sup> may not be adequate. In this paper, a modified method is proposed and some general principles and suggestions to apply this method are discussed.

### OZONE MONITORING

#### A. Concept

Since meteorological conditions are usually different on high ozone days, only the PWDs deduced from windrose on high ozone days are relevant for ozone monitor siting. For cities with adequate coverage of ozone monitors, the PWDs for ozone can be deduced directly from ozone pollution roses. However, for cities without adequate coverage of monitors, the PWDs for ozone will have to be determined indirectly using ozone conducive meteorological conditions.

The approach suggested here is to

1. use the existing data base to establish criteria for "ozone conducive" days.

2. use the identified criteria to extract all "ozone conducive" days for the last 10 years to derive a windrose for potential high ozone days.
3. use the resulting windrose to select the PWDs for ozone monitor siting.

#### B. Criteria for Selecting "ozone conducive" days

A review of 31 US cities (see Table 1) east of the 99 W for 10 warm seasons (May-October) from 1981 to 1990 reveals that three variables have distinct relationship with ozone concentrations: (1) daily maximum 1-hour temperature, (2) morning (7-10 a.m.) and afternoon (1-4 a.m.) winds and (3) mid-day (10 a.m.-4 p.m.) relative humidity (RH). Statistics show that high ozone concentrations are generally associated with high temperatures, low to moderate winds and low mid-day RH. There are significant geographic differences, too. For example, in the North, ozone production is most sensitive to high temperatures, while in the South, low winds and low RH are much more crucial for high ozone.

To select "ozone conducive" days from local climatological data, the values of critical meteorological variables are estimated from the data base with conditional probability, P, satisfying

$$P(y > y_0 | x > c) = .95 \text{ or } .05$$

Where y is a meteorological variable,  $y_0$ , the 5th or the 95th percentile value of y, x, a daily maximum 1-hour ozone concentration variable, and c, a threshold value selected for x. Here, c is selected to be the National Ambient Air Quality Standard (NAAQS) for ozone, 0.12 ppm. For example, given maximum 1-hour ozone concentration to be greater than .12 ppm, the probability for daily maximum temperature to be greater than 80° F is 95 percent.

Following criteria are recommended as a general guide:

1. daily maximum temperature,  $T \geq 80^\circ \text{ F}$ ,
2. morning 7-10 a.m. wind speed  $W_m \leq 10 \text{ kts}$ ,
3. afternoon 1-4 p.m. wind speed  $W_{pm} \leq 14 \text{ kts}$ , and
4. mid-day (10 a.m. - 4 p.m.) relative humidity,  $RH \leq 68\%$ .

These criteria represent, to a great extent, the necessary conditions for daily maximum 1-hour ozone concentrations to exceed the NAAQS as reflected in the 10-year, 31-city data base. While these are conditions necessary for high ozone they are not necessarily sufficient. Other factors such as mixing height, opaque sky cover and topographically induced circulations, etc., may increase characterization of the ozone conducive conditions. However, since the intent of the study is to identify ozone conducive days rather than to predict actual ozone concentrations, this approach is considered to be adequate. Further, as noted above, T,  $W_m$  and  $W_{pm}$ , RH are the most important as well as most accessible variables, and should be considered first.

Since these are general criteria common to all 31 cities in the eastern U.S., local conditions could be a little different and are likely to be more stringent. Refinements to criteria 1-4 above should be made to best reflect local characteristics. For example, to account for climatological differences, higher temperatures should be used in the South. This does not mean

that to produce the same amount of ozone, higher temperature is required in the South than in the North. It is simply because under the same ozone conducive weather system, the temperature rises higher in the South than in the North due to latitudinal effect. Also, away from the transport dominant regions (e.g., the Northeast and the Midwest), the criteria for wind speeds should most likely be lowered to account for the increasing proportion of local ozone production under calm and light wind conditions. Further, due to the high temperatures in the South and plentiful moisture supplied from Gulf of Mexico, the suppression or delaying of the afternoon moist convective activities is crucial for ozone to reach peak values in the Gulf regions. Thus, a relative lower RH is needed for the Gulf regions. As a general guide, the following refined criteria could be applied to broad areas:

- 1a.  $T \geq 80^\circ \text{ F}$  for cities north of  $40^\circ$ ,  
 $T \geq 83^\circ \text{ F}$  for most cities in the continental US,  
 $T \geq 85^\circ \text{ F}$  for cities south of  $30^\circ$ .
- 2a.  $W_{\text{am}} \leq 10 \text{ kts}$  for cities in transport regions,  
 $W_{\text{am}} \leq 8 \text{ kts}$  for cities outside transport regions.
- 3a.  $W_{\text{pm}} \leq 14 \text{ kts}$  for cities in transport regions,  
 $W_{\text{pm}} \leq 12 \text{ kts}$  for cities outside transport regions.
- 4a.  $\text{RH} \leq 65\%$  for cities north of  $30^\circ$ ,  
 $\text{RH} \leq 60\%$  for cities south of  $30^\circ$ .

### C. Constructing Windroses and Siting Monitors

As a starting point, select all days in the last 10 years that satisfy the refined criteria 1a, 2a and 4a as a basis for constructing a morning windrose for ozone and subsequent determination of the morning PWD. Select all days satisfying the refined conditions 1a, 3a and 4a to construct the afternoon windrose for ozone and deduce the afternoon PWD. Over simple terrain areas these two windroses and PWDs should be very similar. However, over complex terrain and coastal areas these two windroses and PWDs could be quite different.

Figure 1 shows examples of windroses derived from ozone conducive meteorological conditions and those derived from ozone concentrations greater than 100 ppb in the 31 cities. From this figure, it is obvious that the PWDs selected from meteorologically conducive criteria are essentially the same as those selected from high ozone days. To further check the robustness of these criteria, the model has been applied to 10 Western cities outside the study domain. An example is given in Figure 2. The similarity of the two wind roses shown in Figure 2 suggests that the model works just as well in the West as in the East. Thus, it is clear that the ozone conducive criteria derived from the 10-year, 31 cities meteorological data are quite robust and may be applied to other cities of the U.S..

Figure 3 demonstrates how the PWDs can be used in siting the monitors. The morning PWD is suggested to be used as a guide to site the upwind background monitor (M1) and to site the maximum precursor emissions monitor (M2). The afternoon PWD is suggested to be used to site ozone monitor (M3) at the downwind fringe of MSA/CMSA and to site ozone monitor (M4) where maximum 1-hour concentrations are likely to be observed. Typically, M1 will be located along the morning PWD 10 to 30 miles upwind from the city limit and M2 will be located along the morning PWD at the downwind edge of the CBD. M3 should be located along

the afternoon PWD at the downwind fringe of the urban area half way between M2 and M4. Typically, M4 should be located along the afternoon PWD 10 to 30 miles from the urban fringe depending on the average the wind speed.

#### **D. Limitations and Suggested Remedies**

In many areas, there are three types of high ozone days: namely, overwhelming transport, weak transport (or mixed transport and stagnation) and stagnation. The windrose concept to site ozone monitors is only applicable to the transport types, but not applicable to the stagnation type. In general, transport types dominate north of 40° N, stagnation type dominates Ohio River Valley and northern Gulf Coast, and a mixture of the two is observed in the rest of the eastern U.S.. In areas where stagnation dominates the high ozone days, a well defined PWD may not be available. If no well-defined PWD can be resolved, use the major axes of the emission sources as the substitutes for PWDs and the ozone monitors should be located along these axes but no more than 10 miles from the urban fringe. The reasons for this choice are two-fold: 1) Completely calm condition seldom last more than an hour during the day. Most stagnation days have light (< 3 kts) but variable winds; 2) Ozone concentrations are likely to be the highest when the winds are along the axis of emissions because precursor concentrations are likely to be highest and dispersion is minimum.

For coastal cities, synoptic winds are generally influenced by the seabreeze or lake breeze circulations. This is typically reflected in the difference of the morning and afternoon PWDs. The maximum-ozone monitors should be located at the downwind side of the resultant winds ( i.e., the vector average of the morning and afternoon PWDs) and the monitors should be located as near as possible to the sea/lake breeze convergence zone.

#### **VOC AND NO<sub>x</sub> EMISSIONS MONITORING**

Exposure to toxic VOC and NO<sub>x</sub> gases is a prime concern. Thus, the use of the prevalent wind directions derived from local climatological data is adequate for siting VOC/NO<sub>x</sub> monitors (M2a) designed primarily to assess exposure to air toxics. It is not surprising that M2 and M2a are likely to be at different locations since meteorological conditions favorable for high VOC and NO<sub>x</sub> concentrations may not be favorable for ozone formation. For instance, NO<sub>x</sub> concentrations tend to be much higher on cold stable winter mornings than on hot summer afternoons when ozone levels are high.

#### **CONCLUDING REMARKS**

Meteorological considerations in siting monitors for photochemical pollutants are discussed. A method using ozone conducive windrose data to site ozone and its precursors monitors has been presented. The ozone conducive criteria derived from 31-city, 10-year meteorological data appear to be quite robust, suggesting that this method may be applicable to site photochemical pollutant monitors in other areas of the US. However, due to the vast climatological and topographic differences across the nation, the suggested criteria should only be used as general considerations for siting monitors of ozone and its precursors. For a better designed ozone monitor network, it is recommended to use any additional credible local data, if available, to better define the local climatological conditions. Many local data may not be reported to the National Meteorological Center data base. Understanding the local micro-climatology and precursors distribution, particularly in the complex terrain area, will greatly help

in finding the best monitor locations.

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***Poster Session***

# ACCUMULATION OF PERSISTENT ORGANIC COMPOUNDS IN SPRUCE NEEDLES IN RELATION TO CONCENTRATIONS IN AIR AND DEPOSITION

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## ABSTRACT

There is an important contribution of persistent organic compounds, POC, to the Swedish west coast via atmospheric transport and deposition. Uptake by plants may play a significant role in the circulation of these compounds in terrestrial environment.

The aim of this study is to obtain knowledge about accumulation of POC in spruce needles in relation to concentrations in air and amounts in deposition (artificial surface). In addition atmospheric contribution of POC to a forest ecosystem at the Swedish west coast can be estimated.

Measurements of POC have been carried out in campaigns during different seasons at an established experimental site, where a forest area is covered with a roof. Needles were collected both outside the "roof" yielding the total deposition and below the "roof" where the main mechanism is gas phase accumulation.

The results indicated that the contribution of POC via deposition from the air to a forest area is similar to that at a coastal station. No differences in the concentrations of HCH, HCB and in the needles were obtained between samples collected during a winter period outside and below the roof but a decrease in the content of particle bound PCB occurred in needles collected under the roof compared to the total accumulation.

## INTRODUCTION

Persistent organic compounds, POC, frequently present in the atmosphere include such classes as polychlorinated biphenyls, PCB, chlorinated benzenes and pesticides such as hexachlorocyclohexanes, HCH. Since most of the POC are chemically stable a considerable long-range transport of these compounds takes place in the atmosphere. <sup>1,2,3,4</sup> They exist in the atmosphere both in vapour phase and bound to particles and the atmospheric life time depends on factors as reactivity, polarity, etc. <sup>5,6</sup>

The main sink mechanism for air-borne POC is through deposition to water, soil and vegetation. The deposition takes place either as dry or wet deposition and includes scavenging of both the particles and the gas phase. <sup>7,8</sup> Deposition fluxes are highly variable and are controlled by factors as chemical composition, water solubility, particles size, atmospheric conditions and type of surface. <sup>5</sup> Surfaces such as water surfaces with is lipophilic micro layer and plant waxes may be good for accumulation. <sup>9,10</sup>

Deposition to plant surfaces occurs through uptake of lipophilic compounds in gas phase, but there may also be a removal in connection with higher ambient temperature or when the concentration in the air decreases. <sup>11</sup> POC with low vapour pressure, which mostly exists in the particle phase in the atmosphere, will also accumulate on the leaf surface. <sup>12</sup>

In terrestrial ecosystems vegetation may play an important role in the circulation and bioaccumulation of POC. <sup>10</sup> In several investigations concentrations in vegetation is used to get a measure of the loading of stable organic compounds in the environment while the content of organic compounds in vegetation may change due to biodegradation, reactions and reemission. <sup>13,14,15</sup>

The aim of this study is to obtain knowledge about the occurrence of POC in spruce needles in relation to the concentration in air and amounts in deposition (artificial surface). The uptake in the needles is studied both as a result of accumulation in gas phase and the total accumulation. In addition, these measurements give information about the contribution of POC to a forest area at the Swedish west coast.

Measurements of POC at background stations at the Swedish west coast have shown that this area receives a significant amount of POC as a result of long-range transport but also due to remission from the sea.<sup>16,17</sup> The compounds studied in this investigation are PCB, HCH and hexachlorobenzene, HCB.

## EXPERIMENTAL

The study was carried out at an experimental site for acidification research, Gårdsjön, in a forest situated about 15 km from the Swedish west coast.<sup>18</sup> At Gårdsjön atmospheric deposition is intercepted of by a transparent plastic roof, 2-4 m above the ground, covering an area of 6300 m<sup>2</sup>. The roofed area includes 370 trees, of 15-25 m height with their crowns above the roof. The roof consists of polycarbonate sheets transmitting 90% of the light.

The sampling of POC was carried out weekly in two campaigns at different seasons, the first Nov. 19 to Dec.12. 1991 and the second May 7 to June 4 1992.

POC in air was collected using a high volume air sampler (HVS), which was placed 2 m above the ground level outside the roof. The sampler was equipped with a glass fibre filter (Grycksbo Munktell 160 MG) for collection of the particles and an adsorbent of polyurethane foam (PUR) for the gas phase. The sampling flow rate was about 20 m<sup>3</sup> hour<sup>-1</sup>. The diameter of the filter and PUR plug was 142 mm and the length of PUR plug 45 mm. Two plugs in series were used to reduce breakthrough. A third back-up plug was used to control the possible breakthrough of POC during the sampling. The PUR-plugs were cleaned before sampling by boiling them in toluene for several hours, followed by Soxhlet-extraction with acetone overnight.

POC in deposition was measured using an open sampler placed 1.5 m above the ground level outside the roof. Both wet and dry deposition was collected with the deposition sampler, which consisted of a 1 m<sup>2</sup> Teflon coated surface with 10 cm high edges. The bottom inclines slightly to a central opening an adsorbent consisting of two cylindrical PUR plugs, 4.5 cm \* 10 cm, which were used for collection of POC in the precipitation. Particles deposited to the surface were rinsed from the Teflon area with ethanol, using a Teflon scraper, and collected in a separate glass bottle. Prior to the sampling the deposition sampler was rinsed with ethanol.

In order to obtain the total accumulation of POC in spruce needles, annual shoots were collected once a week about 1-2 m above the ground from trees outside the roof. Annual needles from twigs under the roof were collected to study the uptake of POC in gas phase. The samples were kept frozen in glass jars until analysis.

### Sample Preparation and Analyses

After sampling filters and adsorbents were Soxhlet-extracted with acetone for 24 hours. The acetone extract was then diluted two-fold with water and extracted twice with pentane/ether 9:1. The extracts were analyzed separately.

The ethanol used for rinsing the Teflon surface of the deposition sampler was filtered twice using Millipore Teflon filters, 10 and 0.5  $\mu$ m, respectively. The filters were then Soxhlet-extracted with acetone for 24 hours and the organic compounds extracted from acetone into pentane/ether as described above. After filtration, the ethanol was diluted with water 1:1 and shaken with pentane/ether as described above. The two organic extracts were then combined.

About 30g needles, fresh weight, were used for the analyses. The samples were Soxhlet-extracted in portion of 10 g each, first with acetone for 24 hours and then with hexane for 24 hours. The acetone extracts were diluted two-fold with 2 % Na<sub>2</sub>SO<sub>4</sub> and extracted twice with

pentane/ether 9:1. The hexane extract was washed with 2 % Na<sub>2</sub>SO<sub>4</sub> and the organic phases were then combined.

Internal standards (2,2',3,3',4,5,5',6,6'-nonachlorobiphenyl and o,p'-DDD) were added to the combined extracts which then were concentrated to about 3 ml and treated with concentrated sulphuric acid (1:1). After removal of the sulphuric acid the extracts were concentrated further and then fractionated on a 2% aluminium oxide column. Three fractions with increasing polarity were collected, pentane, pentane:toluene 95:5, pentane, toluene: ether 45:5:5.<sup>19</sup> In the analytical procedure extraction blanks were used.

The analyses were carried out using a gas chromatograph (Varian 3400) with a SPI injector, equipped with a 50 m capillary column, 0.25 m i.d., 0.25 µm film thickness (CP-Sil-8 CB, Chrompack, Holland) and an electron-capture detector (Ni63). The peak areas were recorded using an integrator (Spectra Physics 4270) and the baselines were corrected using a lab data system (Winner). The concentrations of the chlorinated compounds were adjusted using the internal standards and calculated by comparison to certified standards. The concentrations were also corrected for background from the blank analyses.

Seven individual PCB congeners (IUPAC nos. 28, 52, 101, 118, 153, 138, and 180) were determined and the sum calculated. Three isomers of HCH were determined, alpha, beta- and gamma-HCH.

### Ambient Conditions

Meteorological parameters such as precipitation and ambient temperature are obtained via the Gårdsjö project. Rörvik, a field station on the Swedish west coast, south west of Gårdsjön is a monitoring station within the European Monitoring and Evaluation Program (EMEP). Data via EMEP indicate the level of air pollution to the Swedish west coast.

The meteorological conditions, precipitation and ambient temperature for the different sampling occasions are demonstrated in Table 1. During the first measuring period, Nov. 19 to Dec.12. 1991 the average temperature was rather constant, but the precipitation varied among the different sampling occasions. Data from Rörvik showed that events with increased concentrations of nitrogen dioxide (NO<sub>2</sub>), sulphur dioxide (SO<sub>2</sub>) and soot occurred several times during this period, indicating an influence of air pollutants originating from other countries in Europe (EMEP data).

Some precipitation occurred in the beginning of the second measuring period, May 7 to June 4 1992, but during most of this period the meteorological situation was characterised by dry and warm weather. The level of air pollutants measured at Rörvik may be regarded as normal for this time of the year (EMEP data).

## RESULTS

The concentrations of POC in air, spruce needles and deposition are shown in Table 2. The concentrations of HCB in the air was only measured in the winter samples, G1-G4. Sampling of the air concentrations was not carried out at Gårdsjön during the summer period, G9-G12, while data from Rörvik have been used for the second period.

### Concentrations in Air

The concentrations of PCB in the air was rather constant among the different sampling occasions during the winter period, and the sum of the seven analysed congeners varied between 14-18 pg/m<sup>3</sup>. Higher concentrations of PCB occurred during the summer period, 38-63 pg/m<sup>3</sup>. The concentrations of PCB increased with increasing ambient temperature. The distribution among the different congeners are shown in Figure 1. The PCB components were found almost exclusively in the adsorbent in the summer samples, while in the winter 10-40 % of the congeners 153, 138 and 180 were found on the filters.

Compared to PCB there were greater variations in the air concentrations of HCH among the different sampling occasions in the winter samples. Total concentrations were at the same level for summer and winter samples, but the distribution among the different isomers was quite different.

#### **Concentrations in the Spruce Needles**

An average concentration of 2.6 ng/gTS of the identified PCB was obtained in the needles as a result of total accumulation in the four winter samples, G1-G4. There were only small variations in the PCB concentrations among the different sampling occasions but there were differences between the PCB content in needles collected outside and under the roof respectively, which is demonstrated in Figure 1. The least volatile PCB species were found in lower concentrations in the needles collected under the roof.

The PCB content in the needles collected outside the roof was somewhat lower in the summer samples compared to what was found during the winter period. 1.6 ng/gTS respectively 1.3 ng/gTS of PCB were obtained in the needles collected during the sampling occasion G9-10 and G11-12

The relative distribution of PCB found in the needles outside and under the roof were more similar in the summer samples compared to the winter samples. However higher concentrations occurred in the needles under the roof, especially in the G11-G12 sample.

HCB, which in the atmosphere almost exclusively exist in the gas phase, was present in the same level in all samples but with somewhat higher concentrations in samples collected under the roof. This also to some extent applies to HCH in spite of the greater variations in the air concentrations. However in the summer samples gamma-HCH was present in lower concentrations in the needles under the roof compared to needles outside the roof.

#### **Amounts in Deposition**

The amounts of the PCB identified in the deposition samples G1-G2 varied between 5-8 ng/m<sup>2</sup> day. G3 showed somewhat greater deposition, which probably is an overestimate due to interferences in the analyses of PCB congeners 28, 52 and 101. Smaller amounts of PCB deposition was obtained in the summer samples, 3.5 ng/m<sup>2</sup> day respectively 0.92 ng/m<sup>2</sup> day. The distribution of the PCB congeners in the deposition is demonstrated in Figure 1. The deposition contained relatively more of highly chlorinated PCB compared to the air samples which indicates that a greater share of particle bound PCB are present in the deposition samples. Some co-variation between the amounts of PCB in the deposition and the amounts of precipitation was obtained.

The deposition of HCH varied a lot among different sampling occasions and a significant correlation to precipitation was obtained. The distribution among the isomers was quite different compared to what was found in the air and the needles.

#### **DISCUSSION AND CONCLUSIONS**

Measurements of airborne PCB at an open background station at the Swedish west coast, Rörvik, during winter have shown that the concentration of the seven identified PCB usually is in the level of 20-30 pg/m<sup>3</sup> (Brorström-Lundén unpublished data). The atmospheric concentrations of PCB obtained in the winter samples in the forest area, Gårdsjön, were somewhat lower. The deposition fluxes of PCB obtained at Gårdsjön was higher compared to Rörvik, where an average of 3ng/m<sup>2</sup> day during comparable seasons has been obtained. The atmospheric concentrations of HCH and the amounts of HCH in the deposition were at the same level as those obtained at background stations at the Swedish west coast.

The results in this study indicate that an important contribution of POC, here represented by PCB and HCH, to a forest ecological system at the Swedish west coast may take place due to

deposition. However, up to now only a few measurements have been carried out at Gårdsjön and deposition measured using an artificial surface which most likely affect the deposition velocity differently than natural surfaces, as soil, vegetation and water surfaces.

No accumulation of the analysed compounds in the needles was observed during the two measuring periods. The content of PCB in the needles may be due to uptake of PCB in both gas- and particle phase. The precipitation did not seem to affect the uptake of POC in the needles and no correlation between the concentrations of POC in the needles and the measured deposition was obtained.

The lowest PCB concentrations in the needles were found when the highest concentrations in the air occurred and in connection with the highest temperature, which indicates that the equilibrium between POC in the gas phase and the concentration in the needles probably depends to a great extent on the ambient air temperature.

The higher concentrations of the POC in the needles under the roof compared to the needles outside in the summer samples are not clearly understood. An explanation may be that the concentrations probable will be affected under the roof due to evaporation from the soil and /or a reduction in ventilation.

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**Table 1. Dates for the different sampling occasions, the amounts of precipitation and the ambient temperature.**

SAMPLE	DATE	PRECIPITATION mm	TEMPERATURE C
G1	Nov19-Nov26 1991	4.4	3.0
G2	Nov26-Dec 3 1991	10.5	5.8
G3	Dec3-Dec12 1991	0	1.7
G4	Dec 12-Dec18 1991	22.1	3.9
G9-10	May7-May21 1992	24	11.2
G11-12	May21-June4 1992	0	19.3

**Table 2. Concentrations of POC in air and needles and amounts in deposition for the different sampling occasions**

Sample	G1	G2	G3	G4	G9-10	G11-12
<b>AIR</b>	pg/m3	pg/m3	pg/m3	pg/m3	pg/m3*	pg/m3*
HCB	28	22	44	28	**	**
PCB	18	14	18	17	38	63
HCH	201	74	147	137	198	242
<b>Needles outside the roof</b>	ng/g TS	ng/g TS	ng/g TS	ng/g TS	ng/gTS	ng/gTS
HCB	0.48	0.48	0.48	0.51	0.29	0.41
PCB	2.5	3.0	2.7	2.4	1.6	1.3
HCH	2.6	2.3	2.5	2.6	2.2	2.2
<b>Needles under the roof</b>	ng/g TS	ng/g TS	ng/g TS	ng/g TS	ng/gTS	ng/gTS
HCB	0.55	0.57	0.52	0.65	0.54	0.52
PCB	1.3	1.2	1.2	1.3	2.0	2.3
HCH	2.6	2.5	2.8	3.7	2.0	1.8
<b>DEPOSITION</b>	ng/m2day	ng/m2day	ng/m2day	ng/m2day	ng/m2day	ng/m2day
HCB	0.14	0.22	0.26	0.39	0.20	0.38
PCB	6.14	5.1	9.4*	6.4	3.5	0.92
HCH	1.6	24	1.6	30	14	0.06

PCB = sum of 28, 52, 101, 118, 138, 152 and 180

HCH = alpha-, beta- and gamma-HCH

\* The air concentrations from Rörvik

\*Not determined

Figure 1. The distribution among the different PCB

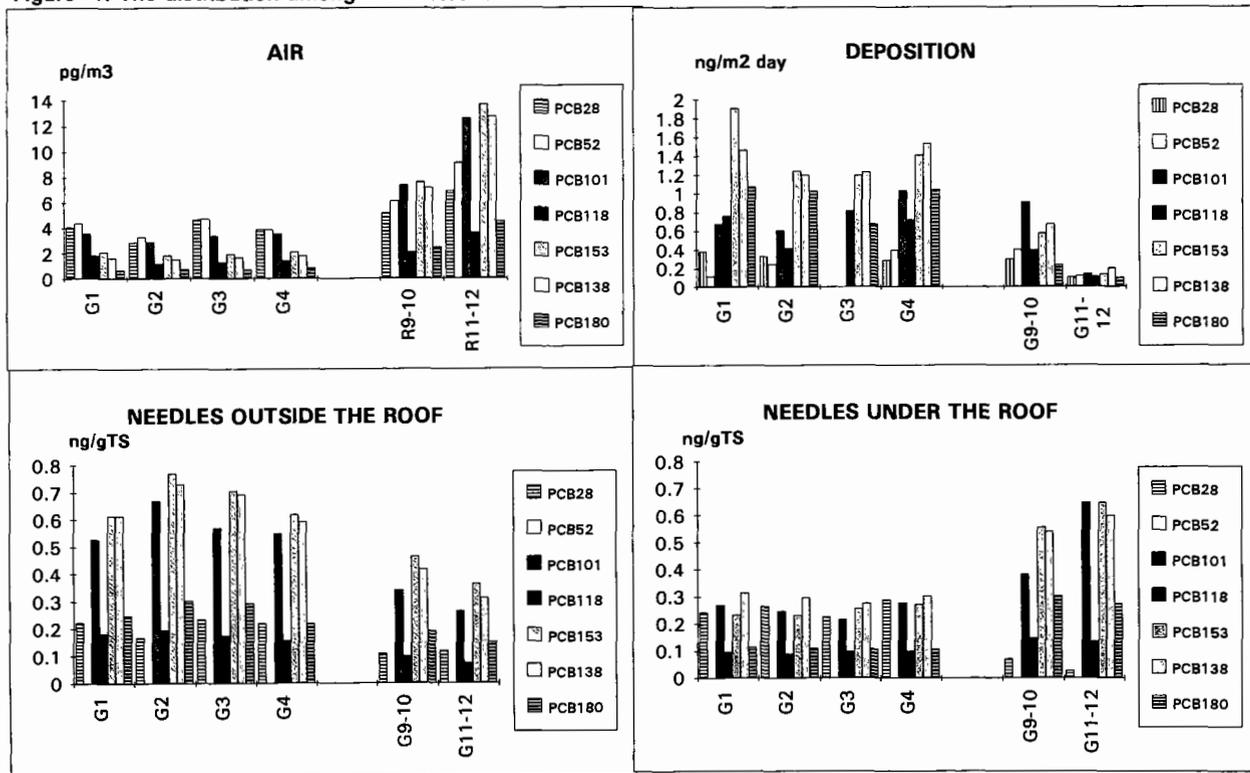
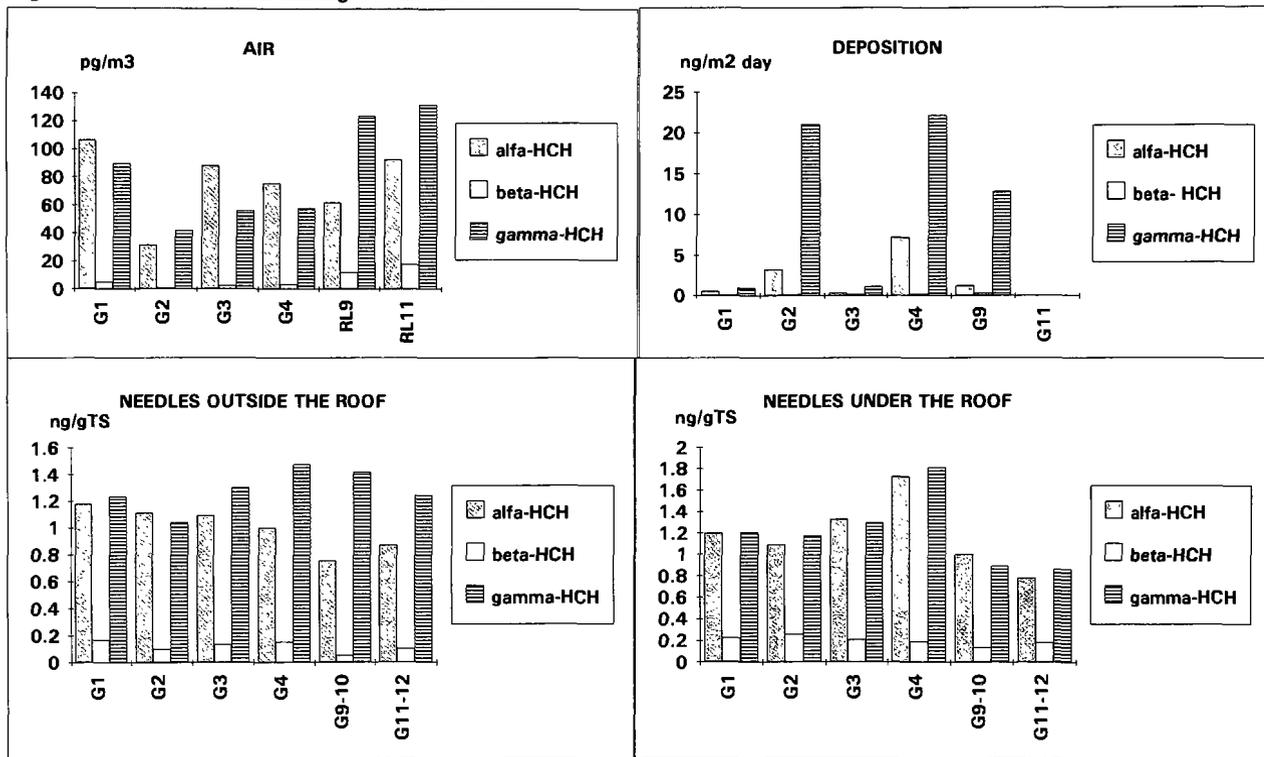


Figure 2. The distribution among the different HCH



# ESTIMATES OF PESTICIDE EXPOSURE FROM THE AGRICULTURAL HEALTH STUDY (AHS)

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## ABSTRACT

Several routes of pesticide exposure to farmer applicators were measured and compared. Whole body (WB) exposure was measured using  $\alpha$ -cellulose patches placed on the outer clothing of the farmer; two measures of hand exposures were taken, one using cotton gloves (GL) and the other using isopropanol handwipes (HA). Inhalation exposures were measured using a PUF cartridge coupled with a personal sampling pump. The three highest exposures received in descending order were: WB > GL > HA.

## INTRODUCTION

The primary goal of the Agricultural Health Study (AHS) sampling program is to provide quantitative measures of pesticide exposure from different farm tasks. In this study, the term exposure is defined as what contacts a person, whether on clothing, skin, or through simple processing by breathing or ingestion. Absorption and metabolism after this contact takes place is not considered here.

## METHODS

All of the methods for collecting the field samples used to assess exposures to pesticides can be found in Harding et al.<sup>1</sup> The analytical methodology used to analyze all field samples can be found in Geno et al.<sup>2</sup>

## RESULTS AND DISCUSSION

### Hygiene, Activity Patterns and Demographics

**Hygiene.** The degree that each farmer practiced good hygiene varied substantially from farm to farm. Farmers 2 and 3 exercised more caution while loading and mixing pesticides. Farmer 2 was the most careful in the use and application of his pesticides. He did not experience any spills or splashes during loading and mixing of the pesticides. When applying the pesticide to his crop, he was inside an enclosed cab. A drift retardant was added to the pesticide application mixture. Farmer 2 also tried to purchase only that amount of pesticide needed for a specific job reducing leftover waste. He did have to stop work to make a five-minute repair on a leaking hose. He wore approximately the same clothing as the other farmers. This included a baseball cap, cotton gloves, a cotton work shirt and pants, and shoes. Farmer 2 washed his hands within 15 minutes after leaving work.

Farmer 3 also exercised good care in handling of pesticides. He wore rubber or leather gloves during all phases of his work. While applying pesticides, he had to stop work for approximately two minutes to repair a nozzle. This farmer also did spraying of hogs inside a barn with an aerosol can. He washed his hands within 30 minutes after leaving work. Farmer 3 was observed eating his lunch in the field, during a work break, without first washing his hands.

Farmer 1A also may have contaminated himself while hosing down some hogs with lindane. Farmer 1A does animal application of pesticides four times yearly. He washed his hands within one to two hours after leaving work.

Farmer 1B poked a hole through a container of alachlor and saturated the finger of one of the cotton gloves he was wearing. This glove was removed because of the chance of high exposure. Otherwise, Farmer 1B reported little hand contact with any pesticides, since he reported that he washed his hands between each loading. Farmer 1B also applied pesticides to animals six times yearly.

All the farmers changed clothes once a day, and their work clothes were washed once every three days.

**Activity Patterns.** All the farmers spend as much as 16 hours in the field during a busy season. Crops can be sprayed every day for up to a two-week period. Farmer 1A reported being active during work and inactive during leisure hours. Farmer 1A had a three year old child. This child's activities were reported for a total period of 70 hours. Out of this total time of 70 hours only one and one-half hours were spent playing in dirt by the child. No hand-to-mouth activity was reported although some probably occurred. While not working, Farmer 1B spent most of his time with his spouse indoors during the monitoring period. The family of Farmer 2 all participated in planting and gardening. The wife of Farmer 2 spent four and one-half hours in the field during the three-day monitoring period. She spent three and one-half hours of this time in the field while pesticides were being applied. The family of Farmer 3 also participated to varying extents in lawn and gardening activities.

**Demographics.** At Farm 1A there was a married couple between the ages of 26 to 45 years old. They had two children, a son approximately one year old and a daughter three years old. Farmer 1B and his spouse were at least 60 years old. Farmer 2 and his spouse were 26 to 45 years of age. They had a 15 year old son and a 13 year old daughter. Farmer 3 and his spouse were 26 to 45 years old and had a daughter eight years old and a son four years old.

### **Occupational Exposure of Farmers During Monitoring Events**

**Hand Versus Inhalation Exposure.** The highest (but not the only) exposures to the hands can occur during accidental spills and splashes, while loading or mixing pesticide, or during repairs on leaky hoses or nozzles. An accidental spill with cotton glove and possible hand contamination did occur on Farm 1B on Day 4 of the monitoring period. This accidental spill at this farm highlights the importance of considering hand exposure. Also, it is unknown whether any of the farmers, while at work, washed their hands before urinating. If not, some pesticide may have been transferred from the hands to the genital area. This is of special concern because of the thin dermal layer of the penis and scrotum through which pesticides will transfer readily.

Table I addresses two issues. One concerns the inhalation exposure (BC, see Table I) received by the farmer during monitored application events. The second is the comparison of total exposure in milligrams received by the hands (HA, see Table I) as compared to the total milligrams sampled in the farmer's breathing zone. It is clear that for those cases for which a TLV (Threshold Limit Value) was available, the farmers' inhalation exposures, while working during the monitoring periods, were far below the TLVs.<sup>3</sup> A similar comparison can be made between the mass of pesticide recovered from the hands and the mass collected by personal air sampling. The mass of pesticide measured on the hands is far greater than that collected by personal air sampling.

Table I. Comparison of handwipe amount to breathing concentration and amount inhaled.

Farm by Event <sup>(1)</sup>	Time (h)	TLV (mg/m <sup>3</sup> )	BC <sup>(2)</sup> (mg/m <sup>3</sup> )	HA <sup>(3)</sup> (mg)	Mass Processed by Inhalation During Work (mg) <sup>(4)</sup>
<b>Alachlor</b>					
1B-3A	3.000	NONE	0.008	6.380	0.043
1B-3B	5.400	NONE	0.011	14.800	0.110
1A-3C	2.600	NONE	0.014	0.480	0.065
1B-4A	3.300	NONE	0.020	9.540	0.120
<b>Atrazine</b>					
1B-3A	3.000	5	0.002	2.000	0.011
1B-3B	5.400	5	0.002	4.330	0.019
1A-3C	2.600	5	0.003	0.113	0.014
1B-4A	3.300	5	0.003	3.76	0.018
<b>2,4-D Isooctyl Ester</b>					
2-3	3.000	NONE	0.001	0.152	0.005
<b>Lindane</b>					
1A-4B	1.100	0.5 (SKIN)	0.001	0.152	0.010
<b>Pyrethrins</b>					
3-4A	0.045	5	0.240	0.450	0.020
<b>Trifluralin</b>					
2-3	3.000	NONE	0.001	0.023	0.005

- (1) All pesticides applied during these events. See Table IV for explanation of coded events.
- (2) BC = The average breathing concentration (mg/m<sup>3</sup>) during the application of pesticides.
- (3) For the HA (applicator handwipe) data, recovery from the skin is unknown. Recovery from the isopropyl-saturated cotton gauze used to take the handwipes was good. Biases in the HA data due to skin absorption or other mechanisms is unknown.
- (4) Calculated by multiplying time (h) \* BC (mg/m<sup>3</sup>) \* 1.8 m<sup>3</sup>/h (see note below).
- TLV Threshold Limit Value (mg/m<sup>3</sup>), defined as that concentration in air that a healthy worker may be exposed to for an eight-hour working period presumably without adverse health effects resulting.

NOTE: A moderate workload was assumed for the farmers with a breathing rate of 1.8 m<sup>3</sup>/h. The personal air samplers were run at 0.23 m<sup>3</sup>/h.

Inhalation exposure is most likely to occur from overspray while the pesticide is being applied to the crops. Some small contribution may be received during mixing and loading.

**Whole Body Exposure Versus Hand.** Another measure of integrated exposure is whole body (WB) exposure. This was calculated using a scaling factor for each farmer. This scaling factor was calculated by first obtaining the surface areas of the farmers' bodies off a nomogram.<sup>4</sup> This required a knowledge of each farmer's height and weight. Next, the total area of the analyzed body  $\alpha$ -cellulose patches was calculated. Then to get the scaling factor the estimated surface area of the farmer was divided by the total area for all three analyzed body  $\alpha$ -cellulose

patches. The results of these calculations are in Table II. To calculate the estimated whole body (WB) exposure, the corresponding body patch concentration was multiplied by the scaling factor to yield a result in milligrams. These results were then compared to the measured mass in milligrams on the cotton gloves as is shown in Table II. Comparing the median values in Table II shows that the estimated WB > GL, but on the same order of magnitude.

Table II. Comparison of whole body exposure to pesticide retained on cotton gloves.

Farm by Event*	DP (mg)	Scaling Factor	Whole Body Exposure (WB in mg)	GL (mg)
<b>Alachlor</b>				
1B-3A	2.05	223	457	105
1B-3B	5.39	223	1022	270
1A-3C	0.38	218	83	59.8
1B-4A	1.02	223	227	>2370 <sup>(1)</sup>
<b>Atrazine</b>				
1B-3A	0.137	223	30	2.37
1B-3B	0.296	223	66	33.2
1A-3C	0.114	218	25	5.25
1B-4A	0.373	223	83	16
<b>2,4-D Isooctyl Ester</b>				
2-3	0.00891	202	1.8	29.3
<b>Lindane</b>				
1A-4B	0.375	218	82	21.2
<b>Pyrethrins</b>				
3-4A	0.023	202	5	2.53
<b>Trifluralin</b>				
2-3	0.00047	202	<u>0.1</u>	<u>0.252</u>
			MIN=0.1	0.252
			MAX=1078	2370
			MEDIAN=67	25.25

\* All pesticides applied during these events.

(1) Finger tip of glove saturated with pesticide.

DP Dermal  $\alpha$ -cellulose patches attached to front of thighs and to the back of the nape of the neck.

SCALING FACTOR: Estimated surface area of farmer divided by total area of all three body  $\alpha$ -cellulose patches.

WB Whole body exposure (mg). WB (mg) = (DP)\*(SCALING).

GL Cotton glove measurements (mg).

**Application Versus Nonapplication Events.** Day 2 at all farms and Day 4 at Farm 2 were baseline days during which no pesticides were applied to the crops. Days 3 and 4 were days during which pesticides were applied to the crops. It is useful to compare the exposures received by the farmers on Day 2 to those received on Days 3 and 4.

It has been shown above that handwipe (HA) data are a good measure of the farmer applicator's exposure. A comparison of application day exposure versus baseline day exposure is given in Table III for the applicator handwipe data. Note that the summary statistics in Table III represents all detected handwipe measurements of all analytes grouped together, separately for application and nonapplication days. The median value for all the measurements taken on application days is four orders of magnitude above baseline days. The maximum for Days 3 and 4 is also much greater than that for Day 2. This indicates an increase in exposure due to pesticide handling and application.

Table III. Farmer handwipe exposure (mg) on application versus nonapplication days.

Percentiles for Nonapplication Days				
10%	25%	50%	75%	100%
0.000015	0.000045	0.000085	0.0029	0.530
N=35				
MIN=0.000015				
MAX=0.530				
MEDIAN=0.000085				
Percentiles for Application Days				
10%	25%	50%	75%	100%
0.00044	0.0162	0.160	3.76	14.80
N=18				
MIN=0.00044				
MAX=14.80				
MEDIAN=0.16				

### CONCLUSIONS AND RECOMMENDATIONS

The three highest exposures received in descending order were: WB > GL > HA. The exposure to the whole body (WB) was comparable to the cotton glove (GL) data. Both represent an integrated average over the work period. WB exposure is an estimated value which assumes the sampled dermal patch areas are representative of exposures received by all body surfaces. GL exposure is calculated from direct measurements. Because WB exposure is an estimated value, this tends to lessen the confidence in the results. GL data may be superior to WB estimated values, but there were problems with the collection of the GL data. The cotton gloves either were poor fitting or restricted the farmer in his ability to do his job effectively.

Greater care in exercising good hygiene practices could substantially reduce the farmer applicator's exposure as well as that of their families. Such practices could include: cautious handling of pesticides, developing proper hand washing habits, removing shoes prior to entering the home, bathing immediately after work, and washing work clothes separately in cold water.

Table IV. Event ID code.

Farm ID	Week Monitored	Sampling Period/Event
1A	Week 1	2 – Day 2
1B	Week 1	3 – Day 3
2	Week 2	3A – Day 3, 1st event/sample
3	Week 3	3B – Day 3, 2nd event/sample
		4 – Day 4
		4A – Day 4, 1st event/sample
		4B – Day 4, 2nd event/sample

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# **SAMPLE COLLECTION METHODS TO ASSESS ENVIRONMENTAL EXPOSURE TO AGRICULTURAL PESTICIDES**

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## **ABSTRACT**

A variety of sample collection media and methods were utilized to assess the environmental exposure of farmers and their families to agricultural pesticides including application events. Collection media included a PUF (polyurethane) cartridge and quartz prefilter, cotton gloves, and  $\alpha$ -cellulose patches, and handwipes. Low levels of some target compounds were detected on media field blanks. Field spikes of sample media showed mean recoveries from 59 to 85%. Collocated PUF cartridges and dermal patches were usually in close agreement. The methodologies utilized performed adequately to collect different sample matrices for assessing pesticide exposure.

## **INTRODUCTION**

One of the objectives of the method evaluation phase of the NCI/EPA Agricultural Health Study (AHS) pilot program was to evaluate the proposed multi-media sampling design.<sup>1</sup> A number of sample collection media and methodologies were incorporated into the study design with the primary objective to evaluate exposure of farmers and their families to agricultural pesticides. Some of the criteria for methodology evaluation from the sampling perspective included ease of use by field personnel, potential impact on the way the farmer performed his daily activities, and adequacy to ascertain exposure through the route monitored. This pilot study was conducted on four farms in Minnesota during the spring of 1992.

## **SAMPLE COLLECTION METHODS**

The multi-media design for environmental exposure incorporated four types of sample media to monitor the farmer's direct exposure, two types of sample media to ascertain residential exposure for the farmer's family, and two methods for the collection of samples to explore exposure through track-in of contaminated soil. The farmer's exposure was monitored with an air sample for inhalation exposure, body patches for body dermal exposure, and gloves with a subsequent handwipe for hand dermal exposure. Evaluation of residential exposure was accomplished with air monitoring at both indoor and outdoor locations and with handwipes on children in the farmer's household. The track-in phenomenon was explored by collection of surface soils in pathways and carpet dust from the interior of the farmhouse. The exposure samples were analyzed by methods described by Geno et al.<sup>2</sup>

### **Personal Exposure Monitoring of the Farmer**

Each farmer was monitored for personal exposure to pesticides via inhalation and dermal routes during farming activities which included both general farm activities not involving pesticides and pesticide application events conducted by the farmer. A pesticide application event included retrieving pesticide formulations from storage, mixing the pesticide with water and other additives to prepare a sprayable mixture, and finally spraying the mixture. The event also included cleanup tasks provided they occurred within the monitoring window. Samples collected included personal air for inhalation exposure, gloves for dermal exposure of the hands, and dermal patches for exposure of other body areas. Additionally, hand dermal exposure was augmented with handwipes collected at the end of each activity period.

The personal air sample collection system consisted of a cartridge (1" diameter by 5" long) containing a PUF plug coupled with a quartz fiber prefilter. The PUF plugs were 22 mm diameter and 7.6 cm long cut from 0.0224 g/cm<sup>3</sup> PUF foam designated as R45. The cut plugs were pre-extracted with acetone for 24 hours, hexane for

48 hours, and then again with acetone for an additional 24 hours. Plugs were dried with a stream of zero nitrogen prior to assembly in the glass cartridge. The filter holder was a nylon Swagelok® union for 1" tubing which held a 25-mm diameter 0.5 µm quartz micro-filter supported by a perforated stainless steel disk. The cartridge assembly was wrapped in aluminum foil and stored in a tall glass jar before and after use. A black shrink tubing sleeve was placed over the cartridge for protection from light and physical damage during use. The cartridge assembly was held in the breathing zone area with a collar clip or Velcro® and coupled with Tygon® tubing to a portable air sampler clipped on a belt. Ambient air was drawn through the cartridge at a nominal 3.8 Lpm (liters per minute) as measured at both the start and end of each monitoring period.

Hand dermal exposure was determined with a pair of all cotton general purpose work gloves with a plain cotton cuff (undyed). The gloves were washed with a brightener-free detergent and pre-extracted with solvents using the same sequence as for the PUF plugs prior to field use. Gloves were stored in glass jars prior to use. Only the farmer would handle the gloves in the jar and would wear the exposure glove under any type of work glove worn as normal practice for farming activities performed during the work day. At the conclusion of the monitoring period, the gloves would be returned to the storage jar.

A set of three dermal patches were used to monitor body exposure. These were located in the center of both thighs and on the nape of the neck and held in place by pinning the patches to the farmer's clothing. The patches were precut to 4" x 4" squares from α-cellulose sheets and backed by an aluminum foil square the same size to isolate the patch from the farmer's clothing. A  $\frac{3}{4}$ " border designated as the handling zone was removed from the patch prior to laboratory extraction.

Handwipes were collected on the farmer at the end of the monitoring day or application period. Two 4" x 4" 6-ply cotton dressing sponges (Johnson & Johnson SOF-WICK) were used directly from the package after each was laced with 10 mL pesticide-grade isopropanol while using the wrapper to hold the sponges. The first wipe was a general wipe of the whole hand while the second wipe was used to more thoroughly wipe each digit. Only the farmer handled the cotton sponges from preparation to placement in the sample container. A 50 mL volume of isopropanol was added to the sample container to initiate extraction prior to receipt in the laboratory.

### **Residential Exposure Monitoring**

Indoor and outdoor 24-hour ambient air samples were collected for three consecutive days (monitoring days 2, 3, and 4) at each farm. The sampling train consisted of the same PUF cartridge system for personal exposure monitoring without the quartz fiber prefilter and holder. The indoor location was an area where the family spent most of their awake time which was generally in or adjacent to the kitchen or family room. The cartridge inlet was placed at a height of 1.0 to 1.2 m which approximates sedentary breathing zone height. The outdoor sampler was placed in an area of outdoor activity, typically where young children would play such as a porch or play area, at a 1.5 m height above ground.

Child handwipes were collected from eligible children (i.e., toilet trained through age 17) at each farm for each application day. The procedure followed that used for the farmer.

### **Surface soil and carpet dust sampling**

Exposure from track-in of contaminated soil was investigated by collecting carpet dust from the interior of the farmhouse and surface soil from three areas where contaminated soil may have been present and potentially tracked in. These areas included the primary entryway to the house used by the farmer, a pathway location between the house and the pesticide mixing or use areas (e.g., fields), and the pesticide storage area or an area adjacent to the mixing area.

The carpet dust was collected from wall-to-wall carpeted areas in each farmhouse using the High Volume Small Surface Sampler (HVS3). Several high traffic areas were identified and then vacuumed with the HVS3 using appropriate setting for the carpet type to obtain a representative sample and sufficient mass for analysis.

The collection technique used for the surface soil samples was dependent on the characteristics of the surface sampled. On hard surfaces, such as concrete walks, steps, or compacted soil, a clean bristle brush was used to sweep

loose soil and dust into a stainless steel pan. If a step off mat was in the sampled area (i.e., the entryway), the soil was collected by turning it upside down and gathering the soil that fell from the mat. Alternatively, if the mat had a solid, yet pliable backing, the mat was rolled into a cylinder, turned vertically, and then gently thumped over a stainless steel catch pan. In gravel areas such as driveways or on bare ground, a clean bristle brush was used to gather the top  $\frac{1}{8}$ " (2 mm) of loose soil.

### Application events

Two types of application events were monitored: (1) spraying post-emergent herbicides to crops using a ground boom sprayer, and (2) applying insecticides in livestock operations. Table I summarizes the herbicide application events monitored at each farm. Since the farmer did not significantly change formulations during the monitored events, the herbicide mixture information applies to all events monitored at that farm.

Table I. Summary of herbicide application events.

Farmer-Event	Period (h)	Volume (gals)	Herbicide/Mix Ratio	Purpose
1B-3A	3.0	300	Lasso® (alachlor)	Control weeds in corn
1B-3B	5.4	600	6 gal/300 gal	
1A-3C	2.6	300	Marksmen® (dicamba, atrazine)	
1B-4A	3.3	300	3 $\frac{1}{4}$ gal/300 gal	Control of broadleaf weeds on nonharvestable wheat crop
2-3	3.0	500	LV-4® (2,4-D isooctyl ester) 5 gal/500 gal	
3-3	7.0	2750	Pursuit® (imazethapyr)	Control weeds in soybeans
3-4B	7.2	1600	100 oz/500 gal	

Two distinctively different insecticide applications are monitored. Both were for control of insect problems in hog raising operations, but the specific purpose and method of application were dissimilar. The exposure of the farmer was monitored with the same methodologies as for the herbicide applications.

Farmer 1A applied lindane with a garden style hose sprayer for control of mange mites on hogs. Lindane was added to the mixing container on a hose sprayer which was then applied directly to hogs as an aqueous stream containing approximately 0.06% lindane.

Farmer 1B used a natural pyrethrin aerosol spray to control flies in a hog barn. The spray was released in a manner that created a fog within the barn which was enhanced since doors were closed to minimize ventilation. Approximately one third of a 32 oz. commercially available can was released in four rooms of the barn for a period of 2.7 minutes.

### **SAMPLE COLLECTION QUALITY CONTROL RESULTS**

Field blanks, field spikes, and collocated duplicates were used to evaluate the contamination potential, accuracy, and precision of the sampling data. Results for detected target compounds are reported in the following sections.

#### **Field Blanks/Background Levels**

Results from the analysis of field blank samples for five matrices are presented in Table II. Nanogram levels of target analytes were detected in every field blank matrix: PUF plug, PUF plug and quartz filter, glove pair, isopropanol-laced cotton sponge dressings used for handwipes, and the  $\alpha$ -cellulose patches used as body patches. Each field blank matrix was prepared in the same batches as the corresponding field sample matrix. Field blanks were exposed to the same set-up and take-down steps as field samples. Thus, for neutral target pesticides, similar levels may be attributable to brief exposure to surface residues through handling during sample set-up or take-down on the farm.

Table II. Results of field blank analyses by matrix (ng/sample).

Analyte	PUF	PUF + Filter	Glove Pair	Cotton Dressings		$\alpha$ -Cellulose patches
				1	2	
<b>Neutral Pesticides</b>						
Alachlor	7	NA	NA		NA	NA
Atrazine	78	NA	NA	36	NA	NA
Captan		NA	NA	11	NA	NA
Chlordane:alpha+gamma	1	NA	NA	6	NA	NA
$\Sigma$ DDT=DDT+DDD+DDE		NA	NA	31	NA	NA
Diazinon	3	NA	NA		NA	NA
Lindane		NA	NA	2	NA	NA
Metolachlor	3	NA	NA		NA	NA
Propoxur		NA	NA	32	NA	NA
<b>Acidic Pesticides</b>						
2,4-D	3			147	350	
Dicamba	1	13	16	8	23	28
Pentachlorophenol			1	33	4	1
Imazepathyr	NA	NA	370	NA	NA	63

NA = Not analyzed

#### Field Spikes

Field spikes of eight target pesticides (six neutral and two acidic pesticides) were generated from three PUF cartridges and from two isopropanol-laced cotton sponge dressings used for handwipe sampling. Spiked samples were generated in a clean field setting by spiking a known microvolume of a solvent-based spiking solution onto clean sample media. The same sample handling protocol was followed after spiking as used with actual field samples.

The average recovery and standard deviation of the field spike results for the neutral pesticides in relation to the data quality objective of 75% are presented in Table III. Recovery of atrazine, chlorpyrifos, and diazinon from PUF exceeded 75%, whereas recovery of alachlor,  $\gamma$ -chlordane, and propoxur were somewhat lower. Field spike recovery of chlorpyrifos, diazinon, and propoxur from the handwipe matrix exceeded 75%, while recoveries of alachlor and atrazine were slightly lower with  $\gamma$ -chlordane being the lowest of the neutral pesticides.

Table III. Percent recovery of field spikes (mean  $\pm$  standard deviation).

Spiked analyte	Data quality objective	PUF plug (air) (n = 3)	Cotton gauze (handwipe) (n = 2)
Alachlor	$\geq 75$	66 $\pm$ 5	71 $\pm$ 2
Atrazine	$\geq 75$	84 $\pm$ 8	71 $\pm$ 8
$\gamma$ -Chlordane	$\geq 75$	67 $\pm$ 3	64 $\pm$ 0
Chlorpyrifos	$\geq 75$	85 $\pm$ 15	82 $\pm$ 2
Diazinon	$\geq 75$	82 $\pm$ 16	83 $\pm$ 4
Propoxur	$\geq 75$	59 $\pm$ 3	80 $\pm$ 20

### Sample Duplicates

Collocated sample duplicates of PUF cartridges and  $\alpha$ -cellulose patches were collected to estimate sampling precision. Results are summarized in Table IV for three pairs of duplicate 24-hour air sample concentrations. The duplicate air concentrations of target pesticides were usually in close agreement, with ratio, larger/smaller air concentration, no larger than 1.5 in 24 (75%) of 32 duplicate pairs.

Table IV. Duplicate air sample concentrations (ng/m<sup>3</sup>).

Analyte	Farm 2 Indoor Air		Farm 2 Outdoor Air		Farm 3 Indoor Air	
	Primary	Duplicate	Primary	Duplicate	Primary	Duplicate
<b>Neutral Pesticides</b>						
Alachlor	6.2	14.3	4.0	1.9	13.6	13.2
Aldrin				0.3		
Atrazine	6.9	17.2	4.8	2.9		2.0
Captan	0.6					
Chlorpyrifos	13.2	10.6	0.4	0.4	3.4	3.4
2,4-D Isooctyl ester	1.7	2.1	21.1	19.0	NA	NA
$\Sigma$ DDT=DDT+DDD+DDE	0.2				0.2	0.3
Dacthal	0.3	0.3				
Diazinon					5.8	
Dichloran	0.6	0.3	0.1		0.2	0.2
Dieldrin				0.3	0.2	0.2
Folpet	0.7	3.3	1.1	1.6	2.0	2.4
Heptachlor		0.6				
Lindane	2.7	2.9	0.3	0.4	3.1	3.5
Propoxur			0.8		19.5	17.9
Trifluralin	28.7	29.3	12.8	14.3	0.8	0.8
<b>Acidic Pesticides</b>						
2,4-D	2.5	2.5	1.4	0.6	0.8	0.3
Dicamba					0.6	0.6
Pentachlorophenol	0.6	0.9	0.3	0.3	1.1	1.4

NA = Not analyzed

Farmer 3 wore two sets of dermal patches above his clothing on both thighs and between his shoulders beneath the nape of the neck during the imazepathyr application event on day 3. The results are reported in Table V for the collocated duplicate dermal patch samples which were formed by combining alternate patches from the three locations. The paired dermal patch amount ranged from no difference (3 ng each) for pentachlorophenol, through two-to-three-fold difference for 2,4-D and dicamba, to a ten-fold difference for imazepathyr. As expected, dermal patch amounts exhibited more variability than 24-hour fixed location air concentrations.

Table V. Duplicate dermal patch sample amounts from Farmer 3 ( $\mu\text{g}/3$  patches)

	Primary	Duplicate
<b>Acidic Pesticides</b>		
2,4-D	0.170	0.073
Dicamba	101	29.4
Pentachlorophenol	0.003	0.003
Imazethapyr	0.35	3.67

## CONCLUSIONS

In general all the sample collection media and methodologies performed adequately to collect the respective sample matrix for assessing exposure of individuals to pesticides. Specific observations for each of sample media follows.

- The PUF cartridge continues to be a suitable media to collect air samples for inhalation exposure.
- The use of a pre-filter as part of the air sampling train depends upon the sampling environment and target analyte, but the filter must be supported while in the holder, especially when used for personal exposure monitoring.
- The limited number patches may not accurately estimate body exposure and more patches appropriately placed should be used to assess this exposure.
- Gloves for hand dermal exposure may not accurately estimate hand exposure since parts of the glove may become saturated through accidental contact with the pesticide or work habits may be influenced if gloves are not normally worn or if normal work gloves are worn over the exposure gloves.
- The isopropanol-laced cotton dressings used as handwipes demonstrated a simple way to collect hand dermal exposure samples from the farmer and also from young children.
- The collection methodologies utilized for carpet dust and surface soil samples were simple to perform if track-in is investigated.

## ACKNOWLEDGEMENTS

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# COMPARISON OF TRANSFER OF SURFACE CHLORPYRIFOS RESIDUES FROM CARPET BY THREE DISLODGEABLE RESIDUE METHODS

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## ABSTRACT

Experiments were performed to compare transfers of dried chlorpyrifos residues from carpet by the Dow drag sled, the California cloth roller, and the Southwest Research Institute polyurethane foam (PUF) roller. On plush nylon carpet, mean chlorpyrifos transfers were 4.5% by the cloth roller, 1.1% by the drag sled, and 0.65% by the PUF roller. On level-loop polypropylene carpet, mean transfers were 2.5% by the cloth roller, 1.4% by the drag sled, and 1.2% by the PUF roller. The cloth roller was found to be less suitable than the other methods because its transfers exhibited greater variability and were altered by orientation of the roll relative to the lay of the carpet fibers. Moistening the sampling media increased the transfer by the drag sled and the PUF roller, but substantially increased the measurement variability of both methods.

## INTRODUCTION

Dermal contact with residues of pesticides applied to carpets and subsequent skin absorption or ingestion through hand-to-mouth activity are routes of human exposure which need better evaluation, especially for young children. The Dow drag sled<sup>1</sup>, the California cloth roller<sup>2</sup>, and the Southwest Research Institute (SwRI) polyurethane foam roller<sup>3</sup> (SwRI invention disclosure #2061, patent pending) are dislodgeable residue sampling methods which have recently been developed to estimate the transfer of a chemical from a contaminated surface to the skin. This paper reports three experiments conducted to determine which of the three methods deployed as currently used by the developer provides the more reproducible and facile transfer of chlorpyrifos residues from carpet:

- Exp. 1. Transfer comparison of the three methods using dry sampling media on new plush cut-pile nylon carpet.
- Exp. 2. Transfer comparison of the three methods using dry sampling media on new level-loop polypropylene carpet.
- Exp. 3. Transfer comparison of the better two methods using both dry and moist sampling media on new plush cut-pile nylon carpet.

## METHODS

Prior to each experiment, the specified virgin carpet and padding were installed in 1 1/2 rooms (1 room for Experiment 3) of an existing 42 ft x 10 ft 3-room trailer.

## Dislodgeable Residue Methods

Relevant characteristics of the dislodgeable residue methods are summarized and contrasted in Table I. The California cloth roller was constructed and the method performed as described by Ross et al. (1991). A soap-washed and precleaned dry 17 in. × 17 in. cloth of percale bedsheets was placed on the carpet and covered with a sheet of plastic. A 2 ft long by 4 in. diameter sewer pipe, filled with 25 pounds of lead shot ballast and wrapped in a sheet of high density PUF, was rolled forward and backward over the plastic/cloth/carpet sandwich ten times. After the 20 passes, the percale cloth was picked up and analyzed.

The drag sled method was performed using the initial configuration described by Vaccaro and Cranston (1990). Briefly, a precleaned dry 4 in. × 4 in. denim weave cloth supplied by B. Shurdut, Dow Chemical Company, was attached beneath foil under a 3 in. × 3 in. plywood block and an 8-lb weight mounted (Figure 1). The sled was dragged once over a 3 in. × 4 ft carpet strip at 6-8 cm/s. After the single pass, the denim cloth was removed for analysis.

The original PUF roller sampler (Hsu et al., 1990) was used for Experiments 1 and 2. A precleaned dry PUF ring (3 in. length, 3.5 in. OD, 1.62 in. ID) was secured on the 8 in. length × 2 in. OD cylindrical 7.2 lb stainless steel roller. The new (October 1992) model of the PUF roller sampler was used for Experiment 3. A precleaned dry PUF ring was secured on the 3 in. length × 1.75 in. OD cylindrical 0.37 kg aluminum roller (Figure 2). The PUF roller was rolled once over a 3 in. × 1.0 m carpet strip at 10 cm/s once in both directions. After the two passes, the PUF ring was slit and removed from the roller for analysis.

In Experiment 3, PUF rings and denim cloth were used which had been moistened with deionized water. A precleaned PUF ring was uniformly moistened with  $5.0 \pm 0.1$  g of water in the laboratory by spraying the ring surface with an atomizer, compressing with a squeeze tool to obtain uniform water distribution, weighing and sealing in a steel canister until use. The sampling surface of the denim cloth was moistened with  $0.5 \pm 0.1$  g of water from the atomizer and weighed just prior to mounting under the drag sled. When moistened at these levels, the PUF ring and denim cloth were observed to produce equivalent moisture trails at method pressure on a glass surface.

## Broadcast Application of Chlorpyrifos and Ventilation While Drying

Broadcast application of chlorpyrifos to test carpeting was conducted by a licensed pest control applicator according to label instructions for flea control treatment. The formulated product, Dursban® L.O. (E.P.A. Registration No. 464-571), which contains 41.5% chlorpyrifos (O,O-diethyl O-(3,5,6-trichloro-2-pyridyl)phosphorothioate), was applied approximately 40 cm above the carpet as a 0.50% aqueous spray (40 mL/3.785 L water) with a hand-held fan broadcast nozzle attached to an air pressurized tank. Application was accomplished in 2 to 3 min.

The trailer was ventilated for 2 h immediately after application. All windows were opened and window air conditioning units were operated in fresh return air mode. During the first 30 min and last 15 min of the ventilation period, both doors were opened and a box fan was operated outside the test room doorway to allow maximum cross ventilation. Air conditioner units were returned to the usual recirculated air mode just prior to sampling and remained on throughout the sampling period of Experiments 1 and 2.

## Experimental Design

Adjacent samples using each compared dislodgeable residue method (with dry and moist media in Experiment 3) and a deposition coupon (2 coupons in Experiment 3) were collected sequentially within a rectangular block of treated carpet. Six replicate blocks were sampled in Experiments 1 and 2; 4  $\frac{1}{2}$  replicate blocks comprised Experiment 3.

Table I. Characteristics of dislodgeable residue methods.

Property	California cloth roller	Dow drag sled	SwRI PUF roller
Sampling medium (material)	Percalé bedsheet (50% cotton, 50% polyester)	Denim weave cloth (predominantly cotton)	Polyurethane foam ring (polyether, 0.029 g/cm <sup>3</sup> )
Surface of sampling medium	Square (42.9 cm) <sup>2</sup>	Square (10.2 cm) <sup>2</sup>	Curved exterior of ring, (OD = 8.9 cm, length = 7.6 cm)
Contact motion	Roll	Drag	Roll
Face (instantaneous contact area pressed through sampling medium)	440 cm <sup>2</sup> = 42.9 cm x 10.2 cm	58 cm <sup>2</sup> = (7.6 cm) <sup>2</sup>	38.6 cm <sup>2</sup> = 7.6 cm x 5.1 cm
Mass exerting pressure through sampling medium	14.4 kg	3.46 kg	3.25 kg; <sup>a</sup> 3.10 kg <sup>b</sup>
Pressure exerted through sampling medium	2,300 Pa = (14.4 kg)(9.8 m/s <sup>2</sup> )/[(0.61 m)(0.10 m)]	5,900 Pa = (3.46 kg)(9.8 m/s <sup>2</sup> )/(0.076 m) <sup>2</sup>	8,300 Pa; <sup>a</sup> 8,000 Pa <sup>b</sup> = (3.10 kg)(9.8 m/s <sup>2</sup> )/[(0.076 m)(0.05 m)]
Sampled carpet area	0.184 m <sup>2</sup> = (0.429 m) <sup>2</sup>	0.093 m <sup>2</sup> = 0.076 m x 1.22 m	0.076 m <sup>2</sup> = 0.076 m x 1.0 m
Number of passes over sampled carpet area	20	1	2
Sampling speed over carpet	0.23 m/s	0.07 m/s	0.10 m/s

a Original PUF roller sampler

b 1992 model of PUF roller sampler

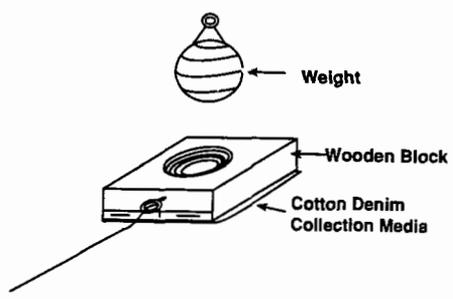


Figure 1. Dow drag sled.

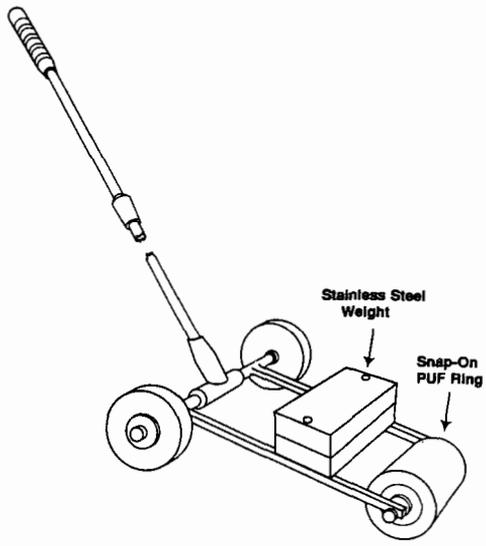


Figure 2. PUF roller sampling instrument.

Deposition coupons, consisting of absorbent alpha-cellulose pads (4 in. x 4 in.) backed with aluminum foil were placed on the carpet prior to the chlorpyrifos application and picked up before the adjacent dislodgeable residue samples from the block were collected. Residues measured on the coupon (pair in Experiment 3) gave an estimate of the surface loading of residue remaining on adjacent carpeting during sampling in the block.

Field blanks of each method were obtained by sampling on the virgin carpet prior to the chlorpyrifos application to assess contamination potential during sampling and handling. Deposition coupon(s) were placed at the designated locations in each sampling block shortly before the application commenced. Field samples were collected in each blocks upon label allowed re-entry, i.e., when the carpet was dry (which was operationally defined as 2 hours after application, but checked by hand contact). The dislodgeable residue samples of a block were collected from specified randomized locations in the block after the deposition coupon(s) were picked up. All samples were collected in one block before proceeding to the next block. Spikes of the precleaned dislodgeable residue media (both dry and moist in Experiment 3) and of a deposition coupon were made both before and after the replicate block sample sets were collected; these field spikes were used to assess and adjust for losses during transport, storage, and extraction.

### Sample Analysis

All samples were Soxhlet-extracted with 6% ethyl ether/94% hexane; extraction commenced within 24 hours after sampling. In Experiment 3, the pair of deposition coupons from a block were extracted together. Extracts were analyzed for chlorpyrifos by GC/ECD on two dissimilar columns and quantitated from the DB-5 column results.

### Data Adjustment

Crude results (mg/sample) from each field sample were adjusted for contamination and extraction inefficiency by subtracting the field blank result and dividing the difference by the mean recovery proportion of the two field spikes for that method. The adjusted result was divided by the sampled carpet area (see Table I) to determine the measured transfer rate (mg/m<sup>2</sup> of carpet contacted) for dislodgeable residue samples and the measured surface loading (mg/m<sup>2</sup>) for coupon samples.

## RESULTS

Recovery of chlorpyrifos in field spikes of all sampling media is shown in Table II. Amounts in field blanks were negligible in Experiments 1 and 3, but within two-to-three orders of magnitude of field samples in Experiment 2, which was performed six days after Experiment 1.

Table II. Percent recovery of chlorpyrifos in field spikes of sampling media.

Sampling medium	Use	Moisture	Field spikes,		Standard deviation
			n	Mean	
α-Cellulose pad	Deposition coupon	Dry	6	94.2	13.9
Denim cloth	Drag sled	Dry	5	102.8	11.0
		Moist	2	96.6	1.6
Percal sheet	Cloth roller	Dry	4	96.2	14.0
PUF ring	PUF roller	Dry	4	110.2	4.6
		Moist	2	107.7	2.1

The surface loading of chlorpyrifos on treated carpets determined at the time of block sampling via deposition coupons is presented in Table III. The chlorpyrifos loading was slightly lower and much more uniform on the level-loop polypropylene carpet in Experiment 2 than on the plush cut-pile nylon carpets in Experiments 1 and 3.

Table III. Chlorpyrifos surface loading<sup>a</sup> on treated carpets during dislodgeable residue sampling<sup>b</sup>.

Experiment: Date	Carpet type	Deposition coupons per replicate	No. of replicates n	Chlorpyrifos loading <sup>a</sup> (mg/m <sup>2</sup> )			Loading coefficient of variation
				Mean	Standard deviation	Range	
1:8/4	Plush nylon	1	6	154.1	94.3	74-329	0.611
2:8/10	Level-loop polypropylene	1	6	120.9	14.0	105-135	0.116
3:11/24	Plush nylon	2	5	183.3	30.6	146-216	0.167

$$a \text{ Loading, mg/m}^2 = \frac{[(\text{deposition amount, mg} - \text{blank amount, mg})/(\text{mean spike recovery})]/(\text{coupon area, m}^2)}$$

The transfer rates of chlorpyrifos from treated carpet by the dislodgeable residue methods are summarized in Table IV. Transfers with dry sampling media were highest for the cloth roller, intermediate for the drag sled, and lowest for the PUF roller, both from plush nylon carpet and from level-loop polypropylene carpet. As shown by the coefficient of variation, all three dislodgeable residue methods gave more repeatable performance on the plush nylon carpet than on the level-loop polypropylene carpet. The cloth roller displayed more variation in chlorpyrifos residue transfer using dry sampling media than did the drag sled and PUF roller, particularly on the plush nylon carpet. Transfers obtained with the cloth roller differed substantially [ $8.1 \pm 1.5$  ( $n=4$ ) vs.  $4.5 \pm 0.1$  ( $n=2$ ) for Experiment 1 mean  $\pm$  std. dev.] for rolls oriented with/against vs. across the lay of the carpet fibers. Transfers with the drag sled and PUF roller did not vary with the orientation of the drag/roll relative to the lay of the carpet fibers. The additional transfer variability observed with the cloth roller is largely attributable to the directional sampling effect.

Transfers using moist media were larger than transfers using dry media for both the drag sled and the PUF roller. However the measurement variability of both methods increased substantially when moist media were used.

The percentage of the chlorpyrifos loading that was transferred by each method in each experiment is presented in Table V. The mean percent transfer of chlorpyrifos residue with the cloth roller on level-loop polypropylene carpet in Experiment 2 (2.5%) was only 55% of its transfer (4.5%) on plush cut-pile nylon carpet in Experiment 1. In contrast, percent transfers with the drag sled and PUF roller were slightly larger on the level-loop polypropylene carpet.

## DISCUSSION

This research was performed to allow intercomparison of dislodgeable residue transfers obtained by recently-developed methods in different studies conducted to support registration of pesticides used in the home. Consequently the cloth roller, drag sled, and PUF roller methods were evaluated as performed by their developers (Table I), despite differences in properties which are likely to affect transfer including sampling pressure and speed, sampled carpet area, and number of passes over the area. The methods were compared upon label-allowed re-entry after application of the pesticide product at the maximum permitted rate, as in pesticide registration studies.

Serious sampling difficulties were experienced in use of the cloth roller method, but not the other methods (Table VI). In particular, the sampling cloth tended to bind and shift from its original position with successive

passes of the roller, so that the actual carpet area contacted by the cloth differed in magnitude and location from the nominal sampled area in an unknown and uncontrollable manner. The variation in transfer with orientation of the passes relative to the lay of the carpet fibers, which was observed only in use of the cloth roller, may relate to the propensity of the cloth to bind and shift during sampling. In situations where the carpet has a distinct lay of pile, especially in areas of traffic, the direction of the drag sled may also affect dislodgeable transfer.

Performance of dislodgeable residue sampling using moistened media may provide a more realistic simulation of transfers experienced by young children who exhibit frequent hand-to-mouth behavior. The goal for moistness of the sampling media is problematic, since the probability distribution of moisture on children's hands is broad and decreases with age. Moistening does increase dislodgeable residue transfer, as expected. However, moistening so exacerbates transfer measurement variability that many more measurements are needed to obtain the precision in mean transfer achieved with dry sampling media.

Mean percent chlorpyrifos transfer obtained from plush cut-pile nylon carpeting declined markedly from Experiment 1 to Experiment 3, both with the drag sled (1.12% vs. 0.44%) and the PUF roller (0.71% vs. 0.26%). The temperature of both the ambient air (Table V) and the room air was higher during sampling in Experiment 1 (performed in August) than in Experiment 3 (in November).

Additional experiments are underway to determine the recovery of residues from the human hand with a handwipe method, and to determine the effect of sampling variables including air temperature on transfers with the drag sled and PUF roller. Future experiments will compare transfers by human hand presses to the dislodgeable residue methods.

Table IV. Comparison of dislodgeable residue method transfer<sup>a</sup> of chlorpyrifos residue by carpet type and media moisture.

Experiment	Carpet type	Dislodgeable residue method	Sampling media moistness	No. of replicates n	Chlorpyrifos transfer <sup>a</sup> (mg/m <sup>2</sup> )			Transfer coefficient of variation
					Mean	Standard deviation	Range	
1	Plush nylon	Cloth roller	Dry	6	6.92	2.20	4.4-10.0	0.318
		Drag sled	Dry	6	1.73	0.29	1.4-2.2	0.168
		PUF roller	Dry	6	1.10	0.26	0.8-1.5	0.238
2	Level-loop polypropylene	Cloth roller	Dry	6	3.00	1.34	1.6-4.9	0.446
		Drag sled	Dry	6	1.66	0.70	1.1-2.9	0.420
		PUF roller	Dry	6	1.43	0.56	0.9-2.3	0.393
3	Plush nylon	Drag sled	Dry	4	0.81	0.34	0.5-1.3	0.414
			Moist	5	1.36	0.98	0.6-2.9	0.718
		PUF roller	Dry	4	0.48	0.07	0.4-0.6	0.141
			Moist	5	3.91	2.02	0.6-5.4	0.517

a Transfer, mg/m<sup>2</sup> = [(dislodged amount, mg - blank amount, mg)/(mean spike recovery)]/(sampled area, m<sup>2</sup>)

Table V. Percent<sup>a</sup> of chlorpyrifos loading transferred by dislodgeable residue method and sampling conditions.

Carpet type	Experiment	Moistness of sampling media	Ambient air range during sampling		Percent transfer <sup>a</sup> (mean ± std dev)		
			Temp (°C)	Relative humidity (%)	Cloth roller	Drag sled	PUF roller
Plush nylon	3	Moist	19-21	24-37		0.74±0.53	2.13±1.10
		Dry				0.44±0.18	0.26±0.04
Plush nylon	1	Dry	28-32	55-67	4.49±1.42	1.12±0.19	0.71±0.17
Level-loop polypropylene	2	Dry	29-32	50-67	2.48±1.11	1.37±0.58	1.18±0.46

a Percent transfer =  $100 \times (\text{dislodgeable residue method transfer, mg/m}^2) / (\text{surface loading, mg/m}^2)$

Table VI. Observations from field use of dislodgeable residue methods.

Strengths	Weaknesses
<p><b>California Cloth Roller</b></p> <ul style="list-style-type: none"> <li>• Simple in design</li> <li>• Inexpensive to build from available materials</li> </ul>	<ul style="list-style-type: none"> <li>• Sampling cloth tends to bind and shift from original position</li> <li>• Plastic bag cover may adhere to PUF sleeve on roller from static</li> <li>• Difficult to operate due to mass of roller</li> <li>• Operator must contact treated surface</li> <li>• Susceptible to added pressure from operator</li> <li>• Transfer affected by roll orientation relative to lay of carpet fibers</li> </ul>
<p><b>Dow Drag Sled</b></p> <ul style="list-style-type: none"> <li>• Simple in design</li> <li>• Inexpensive to build from available materials</li> <li>• Simple to use</li> </ul>	
<p><b>SwRI PUF Roller</b></p> <ul style="list-style-type: none"> <li>• Consistent use across operators due to few variables</li> <li>• Relatively simple to use</li> <li>• Foam roller contact is more like skin contact</li> </ul>	

## CONCLUSIONS

1. The California cloth roller is less practical and more variable than the drag sled and PUF roller methods.
2. Transfers as currently performed by the developer were lowest for the PUF roller, intermediate for the drag sled, and highest for the cloth roller when using dry sampling media on two types of carpet.
3. An interaction in transfer percentage exists between carpet type and dislodgeable residue method. Transfers with the cloth roller are not predictive of transfers with the other methods across different types of carpet.
4. Transfers with moist media are larger and much more variable than transfers with dry media for both the PUF roller and the drag sled.

## ACKNOWLEDGEMENT

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APPLICATIONS OF A CONTINUOUS GAS CHROMATOGRAPH:  
AREA MONITORING, SCRUBBERS, AND STACKS

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ABSTRACT

The marriage of the computer and gas chromatograph has produced a very powerful tool in the field of air toxics analysis. Continuous around-the-clock monitoring is now possible, providing important data to confirm EPA or OSHA compliance, in regard to the concentration of hazardous air pollutants. With the aid of the computer, data acquisition options are limitless. One may wish to do trend reporting, activate alarms, archive data, or all three.

In the plant, the gas chromatograph can cycle between several different work areas, in order to assess chemical exposure levels. Data over an extended period of time can be used to show that the work place is complying with OSHA requirements.

The area of air pollution control is also well served by the gas chromatograph. Gas concentrations at the inlet and outlet of a scrubber can be measured to determine scrubber efficiency.

Finally, the gas chromatograph can be used to monitor stack emissions, in order to ensure that the EPA requirements, stemming from the Clean Air Act Amendments, are satisfied.

For air pollutants which do not lend themselves to easy analysis by conventional continuous emissions monitors, the computerized gas chromatograph is a powerful tool for the environmental scientist or engineer, and the use of this instrument will surely increase as the 21st century approaches.

INTRODUCTION IS GAS CHROMATOGRAPHY BEST FOR YOUR APPLICATION?

This paper is divided into two parts. A discussion of choosing the right gas chromatograph (GC) and its associated equipment, will be followed by a presentation of different types of industrial applications.

First though, you need to establish whether or not your air monitoring needs require a gas chromatograph or some other type of gas monitor. Continuous Emission Monitors (CEMs) are readily available for the most common pollutants (Nitrogen Oxides, Sulfur Dioxide, Hydrogen Sulfide, Carbon Monoxide, Oxygen, etc.). Other gas monitors are available to measure specific compounds in indoor air, with relatively good selectivity and minimum interference from other components. The detectors on these instruments vary. Some

examples are electrochemical cell, semiconductor, photoionization, infrared, ultraviolet, flame ionization, etc.

However, there will be cases when a conventional gas monitor will not suit your needs. There will be instances when a monitor is not available for the specific compound of interest, but a situation more commonly encountered concerns interferences from other components. A conventional gas monitor will do you no good if it is not able to discriminate the analyte gas (the compound of interest) from the other gases in the sample.

The GC has a superior ability to separate the analyte from the other gases in the sample, in order to give an accurate assessment of concentration. For example, many volatile organic compounds (VOCs) emitted as a result of painting, printing, and lamination processes can be analyzed as a group by a total hydrocarbon analyzer or a similar device. However should speciation be required, the gas chromatograph is definitely the method of choice. It is able to provide concentration information for several components during one analysis.

The GC is clearly more expensive and sophisticated than many conventional monitors. In many cases GC is overkill and a conventional gas monitor is the instrument of choice. However, when deemed appropriate, gas chromatography can solve a lot of analysis problems not addressed by CEMs and other similar analyzers.

Let us now assume that your application will require the use of a GC. The following section will aid in equipment selection.

## I. CHOOSING THE CORRECT GC INSTRUMENTATION

The market is full of vendors with automated GC equipment. Brand names will not be discussed, but instead, the purpose of this section is to help identify specific needs for your application, hopefully making the decision of what instrumentation to buy, easier for you.

### A. The Analyte(s), and the Sample Matrix

You first need to establish what compound or compounds will be quantified, and at what concentration levels they are expected to be found.

Now list all the other gases which will be present in the sample, and their expected concentrations. In most cases the sample matrix is air, and the nitrogen and oxygen will not interfere with the analysis. However, in certain cases, compounds of similar molecular structure to the analyte, may cause problems with the analysis, if they are not first identified and dealt with. The

temperature and humidity of the sample matrix are also important to note.

#### **B. The Sample Loop, GC Column, and Detector**

The already established expected concentration levels of the analyte(s) will determine the size of the sample loop used to inject the sample matrix on to the GC column.

The chemical nature of the analyte(s) will dictate what GC column, detector, and GC operating conditions (inject, oven, and detector temperatures, valve timing, etc.) will be used. Techniques involving the use of pre-column backflushing, and column switching can also be added to the system if warranted.

#### **C. The Sampling System**

Gas samples from different areas are drawn to the GC through separate tubes by means of a sample pump. Should long tubing runs be anticipated, a larger pump may be required to achieve sufficient draw. Note that the GC will automatically switch from one sample point to the next for analysis, continuously, 24 hours a day.

Should condensation of the analyte be a possibility (particularly at high concentrations of low boiling analytes), heat traced lines all the way to the GC column should, be utilized. In addition, a particulate filter at the end of each sample line, will prevent contamination from penetrating the tubing or the GC.

#### **D. Calibration**

Proper calibration of the GC is crucial to ensure the collection of accurate data. Calibrations are normally done automatically at set time periods. Calibration gas from a compressed cylinder must be introduced to the GC in a an identical way (same pressures, flows, etc.) the sample from the sampling lines is. Furthermore, the concentration of analyte in the calibration gas should be approximately the same as found in the sampling lines.

#### **E. Computer Operation**

Combining the flexibility of a computer with a high quality gas chromatographic analysis, provides a very powerful tool in the field of air toxics analysis. The computer allows the GC to run unattended for long periods of time, performing continuous monitoring and periodic automatic calibrations.

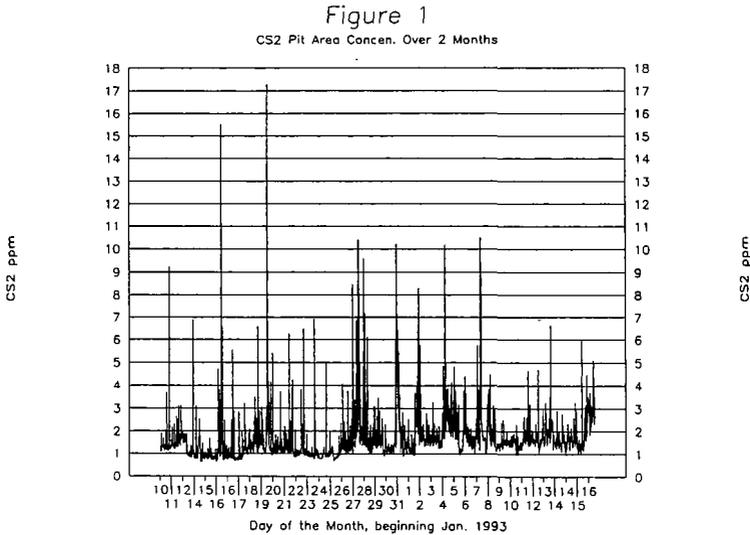
The computer will not only control the GC, but will accept data from it, giving you many operational options. For instance, alarms can be triggered at set concentration levels, trend reporting in graphical form can be presented (see Figures 1 and 2), and data can be stored on disk for future use.

## II. INDUSTRIAL APPLICATIONS OF THE CONTINUOUS GC

Assume now that you have a functional continuous gas chromatograph with sample lines installed. The purpose of this section is to present different applications of the GC, which will benefit operations in an industrial environment.

### A. Area Monitoring

Sample points can be located in work areas in order to assess exposure to the analyte compound. The data generated can be averaged over an 8 hour period to show that the worker is not exposed to levels above those set by OSHA. Figure 1 presents an example of data collected and displayed in graphical form, obtained from a continuous GC monitoring a particular work area.



If the end of the sample line will be exposed to water (from even an occasional water hose down), it should be protected in such a way so that water will never get sucked into the tubing.

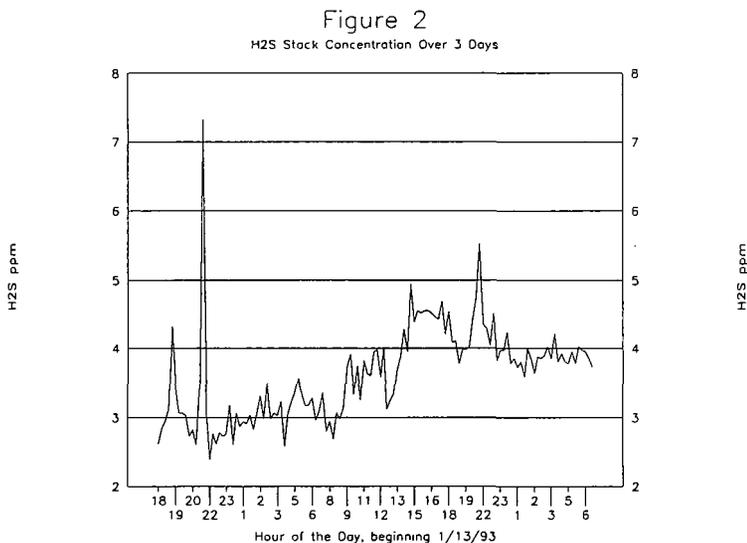
### B. Scrubbers

If the analyte is being scrubbed out of the air in a scrubber, the GC is a nice way to determine scrubber efficiency, by measuring the inlet and outlet concentrations.

A word of caution is warranted about sample conditioning. Often the scrubber air may be very humid, hot, or dirty, and some type of sample conditioning will be required prior to introduction into the GC. Make sure the conditioner does not scrub out some of the analyte, preventing the GC from seeing the true concentration.

### C. Stacks

This is one of the most popular applications of the continuous GC. The Clean Air Act Amendments require strict control of air emissions, and the GC is a tool used to ensure EPA compliance. The previous discussion of sample conditioning applies equally for stacks, and proper precautions should be taken. Figure 2 presents an example of data collected and displayed in graphical form, obtained from a continuous GC monitoring stack emissions.



Should flow rate data be available from a continuous flow monitor in the stack, a combination of the GC and flow data can give a continuous reading of emissions rates (lb/hr) of the given analyte.

### CONCLUSIONS

Continuous gas monitoring can be done by many computerized analytical methods, one of them being gas chromatography. After review of your specific monitoring needs, a properly equipped computer operated GC may be the best alternative in providing the

best analytical data available for your analysis.

Whether it be area monitoring to confirm OSHA compliance, or scrubber/stack monitoring to satisfy EPA requirements of the Clean Air Act Amendments, the computerized continuous gas chromatograph provides the user valuable information for all of these industrial applications.

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# INTERNAL STANDARD IMPLEMENTATION IN AIR MONITORING

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## **Abstract**

Internal standards are routinely employed in many analytical methods to correct for fluctuations in system performance. This Poster Session will first discuss the loop injection technique for introducing internal standards to an air matrix during cryogenic concentration. Secondly, the advantages of using internal standards in the analyses of volatile organics in air will be demonstrated by comparative analyses with external standardization.

## **Introduction**

In many environmental laboratories, analytical instrumentation is operated around the clock to utilize equipment effectively. GC/MS systems in constant use may exhibit changes in sensitivity as the chromatographic column degrades, the ion source becomes dirty and the analyzer electronics age. Any changes in response can be corrected by incorporating an internal standard into the analyses.

The main advantage of internal standards is that the method of quantitation relies on relative response factors rather than absolute area counts. Relative response factors are calculated for each analyte from calibration data as follows:

$$\text{RRF}_x = \frac{(A_x)(C_{is})}{(C_x)(A_{is})}$$

- $\text{RRF}_x$  = Relative response factor for Analyte X  
 $A_x$  = Area of quantitation ion for Analyte X  
 $C_x$  = Concentration of Analyte X (units y)  
 $A_{is}$  = Area of quantitation for Internal Standard  
 $C_{is}$  = Concentration of Internal Standard (units y)

### Internal Standard Introduction

Before incorporating internal standards into the analyses of air samples, the technique for introduction was evaluated. Internal standard addition is performed on the Nutech 3550A cryogenic concentrator by loop injection. The measured volume is independent of the standard vessel pressure, since the loop is allowed to come to atmospheric pressure before the loop contents are transferred to the cryotrap. A precision study of four compounds commonly used as internal standards in other volatile analyses was performed. This data was generated using the Nutech 3550A cryogenic concentrator interfaced with Hewlett-Packard 5890 SeriesII GC/FID. Table I lists raw data area counts for 18 consecutive analyses of the internal standards. Relative standard deviations(RSDs) for this analysis clearly validate the high level of precision (>98%) associated with this particular configuration.

### Comparative Analysis

To illustrate the effectiveness of internal standard quantitation, one set of data files is examined using both internal standard and external standard methods. Data was generated on the Nutech 3550A cryogenic concentrator interfaced with the Hewlett-Packard 5971 GC/MSD. A three point calibration of eight volatile organic compounds (VOCs) in an air matrix was run in triplicate. Bromofluorobenzene was selected as the internal standard. Examination of the data files reveals a trend of decreasing area counts that range between five to ten percent during the twelve hour course of data acquisition.

Table II lists results from external standardization. Reproducibility is good with an average precision of 92% and percent recovery greater than 94%. Table III considers the same triplicate analysis as does Table II, with the incorporation of an internal standard into the quantitation. Percent recovery of analyses from actual concentrations averages 97.3%, a gain of 2.4% over external standardization. Overall precision is two times higher using internal standards as evidenced by the average %RSD of 4.08%.

### **Conclusion**

The data presented here shows the advantages of using internal standards for air analysis. Internal standard quantitation shows two times greater precision than does external standard quantitation. Internal standards allow for better comparison and quantitation of data despite variances in the systems performance. Loop injection proves to be a very effective and consistent means for internal standard introduction.

**TABLE 1: INTERNAL STANDARD LOOP INJECTION PRECISION BY GC/FID.**

DATAFILE	IS #1	IS #2	IS #3	BFB
001F0101	64906	419001	464096	197972
001F0102	64812	420052	464243	197323
001F0103	64884	419779	463047	196659
001F0104	63824	413789	455360	192026
001F0105	63916	413275	452873	189709
001F0106	63943	412562	451748	189047
001F0107	64432	416540	457305	191512
001F0108	64034	413561	453972	190399
001F0109	64556	417270	458086	192392
001F0110	63969	414169	455505	191571
001F0111	64624	417617	459448	193319
001F0112	64509	417753	460215	194187
001F0113	64531	416351	456141	190963
001F0114	64307	415812	457812	193227
001F0115	64076	420588	454389	191108
001F0116	64838	420297	464005	196396
001F0117	64838	418463	461594	194884
001F0118	65533	422836	465264	195986
<b>AVERAGE</b>	<b>64474</b>	<b>417206</b>	<b>458617</b>	<b>193260</b>
<b>Std Dev(n-1)</b>	<b>456.43</b>	<b>2940.65</b>	<b>4306.76</b>	<b>2740.41</b>
<b>% RSD</b>	<b>0.71</b>	<b>0.70</b>	<b>0.94</b>	<b>1.42</b>

**IS #1** Bromochloromethane  
**IS #2** 1,4-Difluorobenzene  
**IS #3** Chlorobenzene-d5  
**BFB** Bromofluorobenzene

**Table 3: Internal Standard Quantitation.**

# Compound	Std Level	Calib 1	Calib 2	Calib 3	Average	% Recovery	Std Dev	%RSD
	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>			
1 Vinylchloride	9.30	8.98	8.70	8.80	8.83	94.91	0.14	1.61
2 1,1-Dichloroethene	11.40	14.36	12.70	10.69	12.58	110.38	1.84	14.60
3 1,1-Dichloroethane	10.50	10.99	9.90	10.10	10.33	98.38	0.58	5.62
4 cis-1,2-Dichloroethene	10.50	10.86	9.80	9.89	10.18	96.98	0.59	5.77
5 1,2-Dichloroethane	10.10	10.40	9.08	9.57	9.68	95.87	0.67	6.89
6 1,1,1-Trichloroethane	10.40	10.86	9.62	9.88	10.12	97.31	0.65	6.46
7 Dibromoethane	10.10	10.33	9.05	9.38	9.59	94.92	0.66	6.93
8 Tetrachloroethene	9.80	10.42	8.87	8.91	9.40	95.92	0.88	9.40
1 Vinylchloride	46.50	47.43	46.16	44.76	46.12	99.18	1.34	2.90
2 1,1-Dichloroethene	57.00	48.39	62.17	52.64	54.40	95.44	7.06	12.97
3 1,1-Dichloroethane	52.50	51.28	49.80	49.90	50.33	95.86	0.83	1.64
4 cis-1,2-Dichloroethene	52.50	51.31	49.90	49.77	50.33	95.86	0.85	1.70
5 1,2-Dichloroethane	50.50	49.74	47.33	48.04	48.37	95.78	1.24	2.56
6 1,1,1-Trichloroethane	52.00	50.72	48.74	49.19	49.55	95.29	1.04	2.09
7 Dibromoethane	50.50	50.01	47.57	48.26	48.61	96.26	1.26	2.59
8 Tetrachloroethene	49.00	47.87	45.42	45.51	46.27	94.42	1.39	3.00
1 Vinylchloride	93.00	94.97	93.42	89.53	92.64	99.61	2.80	3.03
2 1,1-Dichloroethene	114.00	101.62	113.13	109.41	108.05	94.78	5.87	5.44
3 1,1-Dichloroethane	105.00	102.57	102.57	101.91	102.35	97.48	0.38	0.37
4 cis-1,2-Dichloroethene	105.00	103.80	103.28	102.18	103.09	98.18	0.83	0.80
5 1,2-Dichloroethane	101.00	99.47	99.44	100.60	99.84	98.85	0.66	0.66
6 1,1,1-Trichloroethane	104.00	101.96	101.78	102.17	101.97	98.05	0.20	0.19
7 Dibromoethane	101.00	99.65	100.15	100.07	99.96	98.97	0.27	0.27
8 Tetrachloroethene	98.00	94.08	93.73	93.25	93.69	95.60	0.42	0.44
Average						97.26		4.08

**Table 2: External Standard Quantitation.**

Compound	Std Level	Calib 1	Calib 2	Calib 3	Average	% Recovery	Std Dev	%RSD
	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>				
1 Vinylchloride	9.30	8.82	8.93	8.17	8.64	92.90	0.41	4.75
2 1,1-Dichloroethene	11.40	14.13	13.07	9.95	12.38	108.63	2.17	17.55
3 1,1-Dichloroethane	10.50	10.78	10.08	9.38	10.08	96.00	0.70	6.94
4 cis-1,2-Dichloroethene	10.50	10.66	10.07	9.19	9.97	94.98	0.74	7.42
5 1,2-Dichloroethane	10.10	10.22	9.32	8.87	9.47	93.76	0.69	7.26
6 1,1,1-Trichloroethane	10.40	10.65	9.88	9.17	9.90	95.19	0.74	7.48
7 Dibromoethane	10.10	10.14	9.28	8.70	9.37	92.81	0.72	7.73
8 Tetrachloroethene	9.80	10.22	9.11	8.28	9.20	93.91	0.97	10.58
1 Vinylchloride	46.50	47.60	47.18	41.09	45.29	97.40	3.64	8.04
2 1,1-Dichloroethene	57.00	48.58	63.78	48.40	53.59	94.01	8.83	16.47
3 1,1-Dichloroethane	52.50	51.43	50.87	45.78	49.36	94.02	3.11	6.31
4 cis-1,2-Dichloroethene	52.50	51.47	50.96	45.72	49.38	94.06	3.18	6.45
5 1,2-Dichloroethane	50.50	49.87	48.33	44.08	47.43	93.91	3.00	6.32
6 1,1,1-Trichloroethane	52.00	50.89	49.81	45.19	48.63	93.52	3.03	6.23
7 Dibromoethane	50.50	50.19	48.62	44.31	47.71	94.47	3.04	6.38
8 Tetrachloroethene	49.00	48.06	46.47	41.79	45.44	92.73	3.26	7.17
1 Vinylchloride	93.00	96.07	92.38	79.75	89.40	96.13	8.56	9.57
2 1,1-Dichloroethene	114.00	103.59	112.57	97.77	104.64	91.79	7.46	7.13
3 1,1-Dichloroethane	105.00	104.30	101.93	90.82	99.02	94.30	7.20	7.27
4 cis-1,2-Dichloroethene	105.00	105.50	102.67	90.92	99.70	94.95	7.73	7.75
5 1,2-Dichloroethane	101.00	101.09	98.64	89.49	96.41	95.45	6.11	6.34
6 1,1,1-Trichloroethane	104.00	103.69	101.05	90.93	98.56	94.77	6.74	6.83
7 Dibromoethane	101.00	101.21	99.41	89.02	96.55	95.59	6.58	6.82
8 Tetrachloroethene	98.00	95.65	93.11	82.97	90.58	92.43	6.71	7.41
Average						94.90		8.01

# **ASPECTS OF DATA MANAGEMENT FOR AN LDAR PROGRAM**

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## **ABSTRACT**

The Clean Air Act Amendments (CAAA) of 1990 that apply to hazardous air pollutants have produced a set of regulations governing equipment leaks. These regulations were developed through negotiations among environmental groups, state and local agencies, industry, and the U.S. Environmental Protection Agency (EPA). Details of these requirements were proposed in the Federal Register in November of 1992, and proposed in Hazardous Organic National Emission Standards for Hazardous Air Pollutants (HON). Because some states have decided to adopt these regulations before they are mandated by EPA, industry must be prepared to meet the requirements of these regulations.

One of the major outgrowths of these regulations is the need for electronic collection and management of the large amounts of information required to run a successful Leak Detection And Repair (LDAR) program. In developing its own LDAR computer program, International Technology Corporation (IT) has explored many possible methods for gathering field data using bar code readers, punched tags, and data loggers. IT also has investigated the use of personal computers to manage the information.

Timely reporting to meet the requirements of the regulations has also become a key factor in the operation of an LDAR program. IT has worked with many facilities to supply the scheduling, field operation, and data management capabilities needed to comply with these new regulations. This paper will present the operation of a typical LDAR program's data management activities as well as some program options.

## **INTRODUCTION**

The Clean Air Act Amendments (CAAA) of 1990 that apply to hazardous air pollutants have produced a set of regulations governing equipment leaks. These regulations were developed through negotiations among environmental groups, state and local agencies, industry, and the U.S. Environmental Protection Agency (EPA). Details of these requirements were proposed in the Federal Register in November of 1992, and proposed in the HON. These regulations impose a considerable amount of recordkeeping and reporting requirements in regard to the Leak Detection And Repair (LDAR) program that must be performed by the plants that fall under the regulations. To deal with the amount of data that needs to be kept on site, a well-planned and extensive LDAR database is required. Using a computer program to help manage the vast amount of data, as well as the reporting and scheduling, has become necessary to allow the LDAR process to be conducted more efficiently by fewer people. IT has performed many LDAR jobs using a computer program specifically designed to manage LDAR projects. This paper will describe a typical LDAR project and address the major decisions that make

the difference between the success or failure of an LDAR project.

## **INITIAL TAGGING AND DATA COLLECTION**

The initial step in performing an LDAR program is to identify and tag all of the components in a plant that are covered by the regulations. Prior to the physical tagging of the plant, several issues must be addressed. These issues include: what type of tagging and data collection scheme to use, what data are to be collected, and when will the initial data be collected. The initial data collection phase is the most time-consuming process of all phases in an LDAR program, and requires the most accuracy. For this reason, the data must be collected quickly and accurately.

### **Tagging**

Several options are available for physically identifying the components covered by an LDAR program. The scheme that we use most often to identify components consists of assigning each component a unique six-digit number, called a Tag ID. A Tag ID needs to be attached to each component in the plant so that the component can be identified without the P&I drawings. There are several different ways that this can be accomplished: 1) The Tag ID can be converted to a bar code and the bar code attached to the component; 2) The Tag ID can be represented using a punch card code and the punch card attached to the component; and 3) The Tag ID can be stamped into a stainless steel tag and the tag affixed to the component. The most commonly used material to affix a tag to a source is stainless steel wire. The cost is minimal and if properly twisted, it will not be a hazard to plant personnel. Another option is a nylon or plastic tie. Although these types of ties can be used in some cases, the majority of tags are placed in environments that will quickly dissolve the ties or make them brittle. The third type of tie is a lead "head" with a twisted stainless steel wire attached. The wire is threaded through the lead, which is then crimped on the wire to secure the tag. The extra cost of this type of tie can be a concern. In deciding what type of tag to use, we need to evaluate the advantages and disadvantages of each method. We look for a tagging method that is economical, accurate, safe, speeds up data acquisition, and will survive in a hostile environment.

Bar codes will allow us to identify each component quickly and accurately. However, special laminates and bases paper are used to prevent deterioration of the tag and fading of the printed code. These laminates and bases can prove to be quite expensive when applied to tens of thousands of components. Bar codes also require a special bar code reader to interpret the bar code. To accomplish this, the bar code reader is connected to a data logger, which is connected to the Organic Vapor Analyzer (OVA) to record the screening value. The problem with this setup is twofold. One, while the data logger and bar code reader may be intrinsically safe, when you connect the two together the connection between them is not. Second, it is dangerous for the field personnel to carry an OVA, data logger, and bar code reader while climbing a ladder to reach a high source.

Punch tags are small, 2-inch by 4-inch, metal tags that have holes punched in them that represent a Tag ID. To read a Tag ID, the punch tag must be slid into a reader that determines what the Tag ID is based on the pattern of the holes. This option, like the bar codes, allows the Tag ID to be read quickly and accurately. The tags can be purchased relatively inexpensively and are durable enough to survive in a hostile environment. The problem with this method is that the field person would be required to carry the OVA, data logger, and punch tag reader. Also, the punch tags must be inserted into the reader, a two-handed process that can be very difficult for the field person, given the amount of equipment being carried. Once again there is the question of the connections being intrinsically safe.

Stainless steel tags with the Tag ID punched into them are cheap and durable. This option can be used in conjunction with a data logger hooked into an OVA. The connection may be intrinsically safe, and the field person is only required to carry two pieces of equipment. The field person can enter the Tag ID that is on the tag into the data logger and then take the screening value. Although this method does not provide the accuracy that the other two methods do, it can reduce data collection time because

physical contact with the tag is not required. The data logger can be programmed with the Tag ID's that are to be screened as well as check to make sure that a valid Tag ID has been entered.

Most data are currently collected on field sheets. Field sheets require that the field person write all the component and screening information on a form. This option, unlike the above options, does not incorporate electronic data collection and is time consuming and inaccurate.

### **Data Collection**

After determining how to tag the components in the field, we have to decide what data to initially collect for our LDAR program. According to the HON, the following information must be kept at each plant:

- ID numbers of equipment subject to this regulation and a site layout showing the relative location of the equipment
- a table listing the monitoring frequency of each item of equipment
- a list of ID numbers of compressors that have been elected to operate at a reading of 500 ppm or less with the signature of the owner or operator
- ID numbers of pressure-relief devices in gas/vapor service
- date and result of each compliance test, the background reading, and the reading taken at each piece of equipment
- ID numbers of equipment in vacuum service
- ID numbers of instrumentation system
- ID numbers of equipment in VHAP service for less than 300 hours per year
- list of connectors disturbed since the last monitoring period as well as the date and results of the follow-up monitoring
- list of reconfigured equipment since last monitoring period in batch process units
- list of valves and connectors removed from or added to the process unit
- documentation of process stream composition
- identification of screwed connectors
- identification of welded connectors, the date of the weld, and the date of monitoring

The extensive amount of information that must be kept available at a plant site requires a computer program capable of handling the large amounts of data. The Leak Detection And Repair Management System (LDARMS) that we use for LDAR projects requires a minimum set of data to run. This minimum data set is the information that we want to collect in the field. These data include: Tag ID, process unit, component type, manufacturer, service, location, chemical stream, and if it is an exempt component. The LDARMS program also keeps track of a additional component information which can be entered at a later date.

### **COLLECTING THE DATA**

Once we determine how we want to tag a plant and what data we want to collect, the next step is to physically do the tagging and enter the data into our LDARMS program. To collect the data, we normally use two-person teams: one to tag the component and one to collect the initial data and do the initial screening. The other option is to use only one person to go through the plant and tag all the components and collect the component information. This person will then go through the plant a second time to do the screening. Doing this increases the risk that tags will be missed during the screening process. After a days worth of data have been collected, the information is taken back to the office and entered into the LDARMS program. There are two methods for entering the data into the database. If the data were collected using field sheets, a data clerk must go through all of the field sheets and manually enter each record into the database. This is a time-consuming and inaccurate process. A more

accurate and efficient way to enter the data is to use a data logger to collect the data, and then electronically transfer the data into the LDARMS program. By using this method, data-entry time can be reduced from two to three days to five minutes. After the data has been entered into LDARMS, it will be printed out on paper and check-printed for data entry errors. The data are then ready to be processed and output in report form.

## REPORTING REQUIREMENTS

The reporting requirements for meeting the new HON regulation are quite extensive. Each connection (valve, flange, etc.) that is in service for over 300 hours/year using chemicals regulated by the HON will now have to be identified and reported as such to the EPA in an initial statement submitted within 90 calendar days from the applicability dates. The initial statement will contain:

- o process unit identification
- o numbers of each equipment types
- o method of compliance
- o schedule for each phase of the requirements.

The plant technician can no longer go out and check for leaks and 'say' that each connection has been tested. It now must be documented that each connection has been checked and a value recorded for each identification number. This information must be reported to the local agency or EPA on a semiannual basis. The semiannual report will include:

- o process unit identification
- o frequency of monitoring
- o provisions of subpart implemented

For every component type (valves, connectors, pumps, etc.) the following must be included in each monitoring period:

- o number of leakers detected
- o percent leaking
- o total number monitored
- o number not repaired

In addition, an explanation of any repair delays, process unit shutdowns including dates and durations, changes in processes, and performance test results, or any change in monitoring frequency must also be included. If leaks are detected during routine screening, the instrument and operator identification, as well as the equipment ID number, must be recorded. The dates of each attempt at repairing the equipment must be recorded including the method used to repair the component. The component rescreening reading must also be documented. If there is a repair delay, the reason for the delay must be kept on file with the owner or operator's signature. The expected date of repair as well as the date of successful repair will be recorded. Any process unit shutdowns that occur while the equipment is unrepaired also must be recorded.

After each screening period, a report is generated that contains all the information gathered during that period. This report is then kept at the plant site. Without electronic storage of this information, the data collected could easily take up volumes of paper and shelves of space. The screening data must be kept for a period of two years, which also increases the amount of space required for information storage.

In all probability there will be civil penalties for not complying with the requirements of the regulations. Penalties may be assessed for not filing an initial report, or filing an incomplete report, late

submission of any report, incomplete records, failure to maintain records for an adequate length of time, and failure to repair leaks within the specified time. The emphasis on timely submission of reports as well as their completeness makes the handling of massive amounts of information almost impossible without the help of some type of computer program. In response to this demand, several programs have been developed in the past two years. The key to our program is its flexibility and the ease with which the data can be sorted and checked.

### **ROUTINE MAINTENANCE**

The scheduler within LDARMS schedules component screening according to component type. The schedule includes any valves, flanges, pumps etc. that are required to be screened in a given quarter. Once the screening information is entered into the program, a quarterly report is generated that calculates the emissions from fugitive sources for the plant for that quarter. The information from the screenings are used to estimate the emissions using either the stratified method or the correlation equation. This information can then be used in SARA 313 reporting.

### **SOFTWARE PROGRAM MAINTENANCE**

Once the screening information has been entered into the system, additional maintenance must be performed to ensure the integrity of the data in the program. Repairs made to the leaking components must be entered, changes in service of a component must be logged, and any changes in the process units must be tracked. For example, if a line is taken out of one process unit and moved to another process unit and reinstalled, the program must be updated to reflect the changes in location, service, and chemical stream makeup. If the program is not updated, it will incorrectly estimate the emissions and print out the wrong locations on reports. The maintenance of an LDAR software program requires that a considerable amount of time be spent setting up the program correctly, entering the initial data, maintaining the data in the program, and generating reports.

The reports submitted to the EPA are not necessarily good reports for identifying ways to reduce fugitive emissions. A software program must allow the user to access the data in a way that presents information in an understandable form. The information on which emission reduction plans are based on at one site may be completely different from the data that is used at another site. For these reasons, the LDARMS software that we developed allows us, or plant personnel, to sit down at the computer and design a custom report that contains the required information presented in a way that is easy to understand.

### **CONCLUSIONS**

In order for facilities to comply with the proposed HON regulations, LDAR programs will have to be implemented. The basic choices involve the type of tags to be used, the information collected, and the management of this information. Although various tag types can be selected by the plant operator, the information collected is dictated by the regulations. The most efficient way to handle the large amount of information that must be kept on site is to store it electronically. IT has developed the LDARMS program to assist the plant manager in the data management and reporting aspects of an LDAR program. The ease with which the LDARMS program can be adjusted makes it a valuable asset to the plant manager.

## GAS AND PARTICLE PHASE MEASUREMENTS OF ATMOSPHERIC TOXIC POLLUTANTS

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### ABSTRACT

To follow the migration of semivolatile pollutants through the environment, and the atmosphere in particular, it is necessary to know the partitioning of the pollutants between the vapor and the particle phases. Gas and particle (GAP) samplers have been deployed at Point Petre and at Little Turkey Lake to measure organochlorine pesticides such as  $\alpha$ - and  $\gamma$ -hexachlorocyclohexane (HCH) and hexachlorobenzene (HCB). The GAP sampler measurements have shown that the particle fraction of semivolatile compounds in the atmosphere is greater than that which is determined by the high volume samplers which are backed up by polyurethane foam adsorbents. Additionally, the results suggest that the  $\alpha$ - and  $\gamma$ -HCH have unexpectedly higher particle fractions during the summer months. HCB remains constant throughout the year.

### INTRODUCTION

The mandate of the Canada/US agreement on the Great Lakes is to determine the deposition of toxic pollutants, such as  $\alpha$ - and  $\gamma$ -hexachlorocyclohexane (HCH) and hexachlorobenzene (HCB), to the Great Lakes. These semivolatile compounds occur in both the vapor and particle phases in the atmosphere. Thus in order to assess the relative importance of wet and dry deposition, and to follow the migration of these compounds through the environment, it is necessary to know their distribution between the gas and particle phases.

Traditionally, high volume samplers backed up with a polyurethane foam (PUF) adsorbent are used to obtain operationally defined particle and vapor phase measurements. However, due to the pressure drop across the filter and fluctuations in the atmospheric temperature and in the concentrations of the pollutants, some of the molecules may leave the particle surface and become entrained in the airflow. The molecules may, then, either be adsorbed onto the filter itself, or pass through the filter, be trapped on the PUF adsorbent, and be determined (erroneously) as gas phase material. In addition, gas phase molecules may be trapped on the surface of the collected particles or they may be trapped directly on the filter itself.

To circumvent these problems, the GAP (gas and particle) sampler, a multi-annular, diffusion denuder system, was developed. The GAP sampler reverses the traditional sequence of air sampling by collecting the vapor phase first, then the particle phase. The instrument comprises two individual sample collection units which are operated in parallel. Each unit is fitted with a 10  $\mu$ m size selective inlet (SSI). In the "denuder" unit, air passes through the SSI, through a silicone gum/Tenax-coated denuder in which the gas phase constituents are trapped and retained. The particles pass through the denuder and are collected on a glass fiber filter. Adsorbent cartridges containing Florisil are placed downstream of the filter to trap any material which might volatilize from the surface of the particles or which might be associated

with particles which are too small to be trapped by the filter. The second "conventional" unit is identical to the first except that it does not possess a denuder. The "conventional" unit yields the total (gas phase plus particle phase) loading while the denuder unit yields only the particle phase. Thus, by difference, the gas phase portion of a compound may be determined.

The GAP sampler was designed to operate in areas where the ambient target compound concentrations could be described as regionally representative or background in nature. Air sampling was carried out for (nominally) 46 hours. A description and assessment of the GAP sampler has been published<sup>1</sup> as have papers describing its use in various field measurement programs<sup>2-3</sup>.

Field sampling was carried out between 1987 and 1990 near Little Turkey Lake (north of Lake Superior) and at the Canadian master station (established in response to the Canada-US agreement on the Great Lakes) at Point Petre on the north shore of Lake Ontario. The filters and adsorbents were analyzed for  $\alpha$ - and  $\gamma$ -HCH, and HCB.

#### EXPERIMENTAL

Prior to sampling, the denuders were purged with 260°C nitrogen gas for 12 hours, and then cooled. Whatman GF/A glass fiber filters (47 mm) were baked at 300°C, cooled and weighed before and after use. Florisil was heated in batches at 650°C and 60 g portions were transferred to solvent-cleaned glass cartridges for elution with 30% methylene chloride in hexane (MCH) followed by hexane elution. The adsorbent cartridges were dried under vacuum and stored at 135°C in a desiccator until ready for use. The cartridges were capped and transported at -5°C in a portable cooler. Just prior to sampling, the inside surfaces of the SSI and other air sample transfer tubes were rinsed with hexane.

Duplicate or triplicate samples, and field blanks were collected during each sampling period. A Tylan mass flow controller regulated the airflow to 16.7 L/min and the total volume sampled was determined by a dry test meter which had been calibrated against a primary (gasometer) standard.

The Florisil cartridges were extracted with MCH. After adding an iso-octane keeper, the extracts were concentrated to 2 mL for cleanup. The filters were extracted with methylene chloride and concentrated in the same manner as the Florisil adsorbents. Sample extract cleanup was carried out on a 2% deactivated Florisil column containing anhydrous sodium sulphate in the top portion. After elution with MCH, then hexane, the eluent volume, with additional keeper, was reduced to 2 mL and dispensed in septum vials for injection into the GC. An Hewlett Packard 5890 gas chromatograph with autosampler was used for analysis of the samples. Injections were split into two capillary columns of different polarity (Ultra 1 and Ultra 2) and components were detected with <sup>63</sup>Ni electron capture detectors. When the measured results did not agree between columns it was assumed that the higher result reflected the presence of interfering compounds and, the lower of the two results was selected. Differences between the two column results were usually less than 25% and often less than 10%.

#### RESULTS AND DISCUSSION

The detection limits (DL) were found by multiplying the standard deviation (SD) of the recovery efficiency by three and normalizing to a standard air sample volume of 46 m<sup>3</sup>. Quantitation limits (QL) were similarly calculated by multiplying the SD by 10 and normalizing to the same standard air volume. The resulting DL and QL for the organochlorines (OCs) were as follows: for HCB DL=7 pg/m<sup>3</sup>, QL=23 pg/m<sup>3</sup>; for  $\alpha$ -HCH DL=14 pg/m<sup>3</sup>, QL=46 pg/m<sup>3</sup>; for  $\gamma$ -HCH DL=15 pg/m<sup>3</sup>, QL=50 pg/m<sup>3</sup>.

The results of the field measurements for the target OCs are presented in Table I. As anticipated, the vapor phase components of the three OCs were marginally lower than those reported by Bidleman<sup>4</sup> who used the hi-vol sampler method. A measure of the precision between two collocated instruments was obtained by determining the modified median absolute difference (M.MAD) between the samplers<sup>5</sup> and then dividing by the median of the collocated results and expressing the result as a percent. For three collocated samplers, the median absolute difference was divided by the median of the

average result of the three samplers and expressed as a percent. The precision data shown in Table 2 is considered to be extremely good.

Figure 1 shows the log of the concentration versus 1000/Temperature (K) for the HCH isomers and HCB for both Little Turkey Lake and Point Petre. Although the sampling locations are more than 800 km apart, the data appear to be very similar. The slope for  $\gamma$ -HCH is almost identical to that reported by Hoff<sup>6</sup> and clearly supports the hypothesis that the presence of this compound is a result of the heating and cooling of the soils. The virtually flat slope of HCB indicates that it is essentially all in the atmosphere and that there is little bound up in the soils. Hoff<sup>6</sup>, however, did not see any correlation of the  $\alpha$ -HCH with temperature.

Figure 2 shows the vapor phase component as a function of temperature. The lower vapor phase component in summer appeared to contradict the predictions of the Junge theory<sup>7</sup>. If the denuder suffered breakthrough under warm conditions, some of the trapped vapor phase molecules would reach the filter and be determined as particle phase material. However, as reported previously<sup>1</sup>, the denuders showed no breakthrough at 30°C over sampling times exceeding 48 h. HCB and the HCH isomers behave similarly in the denuder system. If the denuder were acting like a chromatographic column, the HCB would pass through the column first, followed by the HCH isomers. Since the HCB does not break through (there is no increase in particle phase at higher temperature as can be seen in Figure 2c), we conclude that the HCH isomers are not breaking through either. Since the phenomenon occurs during both summer periods (1987 and 1990) and at both sites, we must conclude that an increased particle phase component of the HCH isomers during the summer months in the vicinity of the Great Lakes is a real occurrence, and not an artifact of the GAP sampler. Local use of HCH and soil reentrainment may account for the observed increase in particle phase component.

#### CONCLUSIONS

The GAP sampler technique was designed to address the uncertainty associated with ambient air gas/Particle measurements of semivolatile constituents by conventional filter/adsorber methods. It appears that the  $\alpha$ - and  $\gamma$ -HCH have unexpectedly higher particle fractions during the summer months while the HCB remains remarkably constant. In general, the denuder system shows that the particle phase fraction of semi-volatile compounds in the atmosphere is greater than determined by the hi-vol sampler technique.

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Table 1. Total concentrations and vapor-phase components for HCB,  $\alpha$ -HCH and  $\gamma$ -HCH at Little Turkey Lake and Point Petre.

Date	Avg. Temp.	HCB		$\alpha$ -HCH		$\gamma$ -HCH		$\alpha/\gamma$
		Total (pg.m <sup>-3</sup> )	% Vapor	Total (pg.m <sup>-3</sup> )	% Vapor	Total (pg.m <sup>-3</sup> )	% Vapor	
Little Turkey Lake								
87/05/08-10	11.5	97 (2,±3)	92	285 (2,±25)	93	88 (2,±12)	91	3
87/05/10-12	9.4	81 (2,±4)	96	270 (2,±20)	96	80 (2,±1)	93	3
87/05/12-14	10.0	71 (2,±1)	94	310 (2,±10)	92	115 (2,±15)	91	3
87/07/24-26	19.0	79 (2,±12)	94	475 (2,±5)	87	[49] (2,±4)	93	10
87/07/26-28	17.5	91 (2,±2)	96	450 (2,±40)	92	53 (2,±12)	77	9
87/07/28-30	17.9	26 (2,±3)	94	330 (2,±110)	90	[43] (2,±4)	81	8
87/10/20-22	1.4	76 (2,±5)	100	200 (2,±10)	100	[23] (2,±3)	100	9
87/10/22-24	0.9	68 (2,±8)	100	210 (2,±0)	100	[26] (2,±0)	100	8
87/10/24-26	2.0	75 (2,±2)	100	180 (2,±20)	100	[29] (2,±2)	100	6
Point Petre								
88/11/08-10	11.2	82 (3,±4)	93	150 (3,±10)	88	[18] (3,±5)	100	8
88/11/10-12	8.0	74 (3,±13)	96	103 (3,±6)	100	[11] (3,±6)	100	9
88/11/12-14	9.4	81 (3,±17)	99	122 (3,±28)	100	[16] (3,±9)	100	8
88/11/22-24	1.6	39 (3,±10)	98	100 (3,±0)	100	[8] (3,±0)	100	13
88/11/24-26	3.9	58 (3,±14)	92	117 (3,±6)	100	[15] (3,±6)	100	8
88/11/26-28	8.3	82 (3,±11)	97	330 (3,±36)	94	[15] (3,±1)	100	20
89/03/15-17	-1.4	87 (3,±10)	100	71 (3,±13)	97	[12] (3,±7)	100	6
89/03/17-19	-4.9	57 (2,±3)	96	60 (2,±0)	100	[34] (2,±5)	100	2
89/03/19-21	-1.3	79 (3,±13)	98	59 (3,±7)	100	[8] (3,±0)	100	7
89/11/06-08	4.1	88 (2,±12)	89	145 (2,±15)	95	[13] (2,±3)	100	11
89/11/08-10	6.1	94 (2,±7)	85	140 (2,±10)	100	[11] (2,±3)	100	13
89/12/07-09	-9.5	110 (2,±10)	83	145 (2,±5)	100	ND (2,)	-----	----
89/12/09-11	-3.5	86 (2,±5)	93	85 (2,±7)	100	ND (2,)	-----	----
90/01/23-25	0.2	60 (2,±3)	100	ND (2,)	-----	ND (2,)	-----	----
90/01/25-27	0	93 (2,±3)	100	ND (2,)	-----	ND (2,)	-----	----
90/08/13-15	17.9	125 (2,±15)	90	325 (2,±25)	82	127 (2,±44)	43	2.5
90/08/15-17	20.7	130 (2,±0)	90	235 (2,±5)	73	104 (2,±27)	47	2.4
90/08/27-29	20.1	120 (2,±10)	88	122 (2,±38)	95	59 (1,)	93	2.0
90/08/29-31	17.5	77 (2,±2)	92	66 (2,±1)	81	23 (2,±1)	82	2.9
90/09/17-19	9.9	43 (2,±7)	100	79 (2,±2)	90	27 (2,±0)	27	2.9
90/09/19-21	10.9	58 (2,±4)	99	61 (2,±9)	94	[8] (1,)	100	7.6

The first number in parentheses is the number of replicate measurements and the second is the range (for duplicates) or standard deviation (for triplicates) of the measurements. The values in square brackets are above the detection limit but below the quantitation limit.

Table 2. Precision (%) for duplicate and triplicate sampling measurements of three organochlorines at Little Turkey Lake and at Point Petre.

Location	HCB	$\alpha$ -HCH	$\gamma$ -HCH
Little Turkey Lake (duplicate measurements)	9.66	12.9	17.3
Point Petre (triplicate measurements)	15.3	7.2	25.5

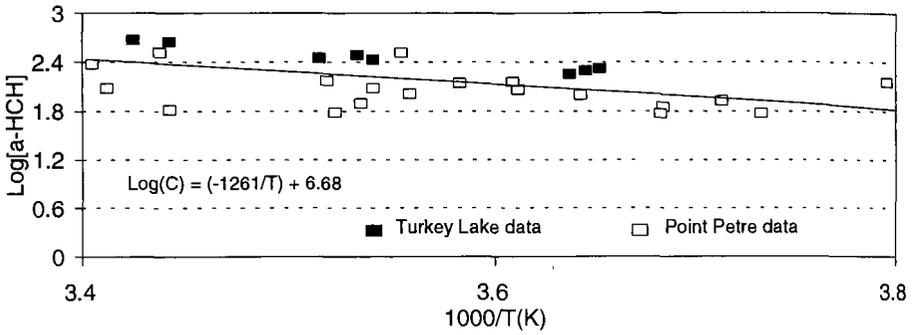


Figure 1a.  $\text{Log}[a\text{-HCH}]$  vs  $1000/T(\text{K})$

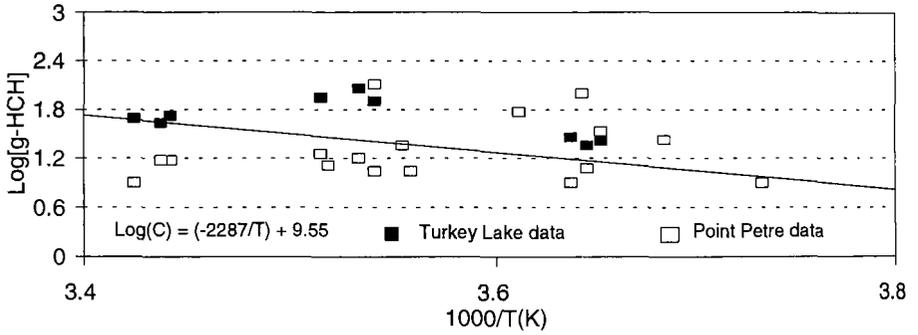


Figure 1b.  $\text{Log}[g\text{-HCH}]$  vs  $1000/T(\text{K})$

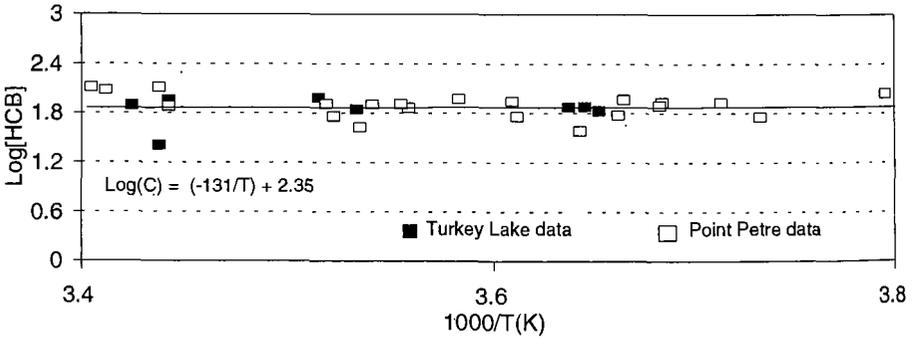


Figure 1c.  $\text{Log}[\text{HCB}]$  vs  $1000/T(\text{K})$

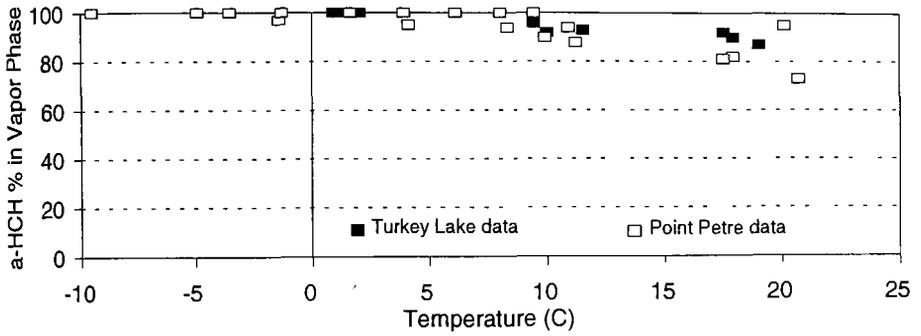


Figure 2a. a-HCH (% in Vapor Phase) vs Temperature

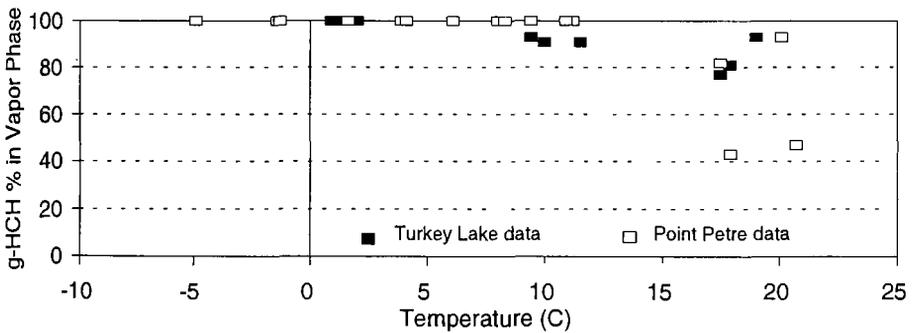


Figure 2b. g-HCH (% in Vapor Phase) vs Temperature

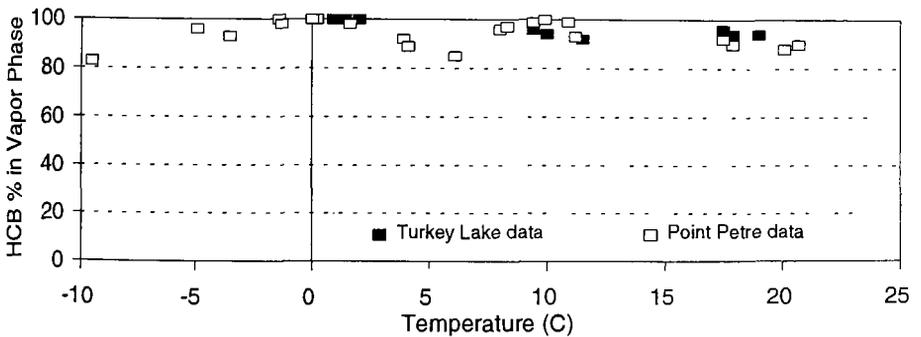


Figure 2c. HCB (% in Vapor Phase) vs Temperature

**EVALUATION OF POLYNUCLEAR AROMATIC HYDROCARBONS AND  
NITROGEN HETEROCYCLES IN THE STACK EFFLUENT OF  
ASPHALT PROCESSING PLANTS**

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**ABSTRACT**

The Connecticut Department of Environmental Protection (CT DEP) conducted stack effluent monitoring at several asphalt plants during 1991 and 1992. The samples were collected in accordance with US EPA SW846 Method 0010 and analyzed by high resolution gas chromatography/ high resolution mass spectroscopy (HRGC/HRMS).

The HRGC/HRMS methodology was developed by Triangle Laboratories, Inc. of Research Triangle Park, North Carolina to satisfy CT DEP's monitoring objectives. These objectives included determining the feasibility of monitoring and simultaneously analyzing for both polynuclear aromatic hydrocarbons (PAH) and nitrogen heterocycles (NHC) in asphalt plant stack samples. The list of target PAHs was developed by CT DEP to help better define its polynuclear aromatic hydrocarbon regulations.

The test results show that seven compounds from CT DEP's targeted list of PAH comprise 98-99% of the identified PAH emissions from asphalt plants. CT DEP reviewed data from oil and natural gas-fired batch operations as well as natural gas-fired batch and express plant operations. Comparisons of the results were made.

**INTRODUCTION**

The Connecticut Department of Environmental Protection (CT DEP) conducted stack emissions monitoring at several asphalt plants during 1991 and 1992. Two types of plants at the Balf Company were tested as part of a USEPA High Risk Point Source (HRPS) Study to determine qualitatively and quantitatively the PAH and NHC emitted from asphalt plants. CT DEP intended to use the PAH emissions data to regulate a specific source as well as support a revision of the existing, but inadequate PAH regulation.

At CT DEP's request two additional plants were tested. The Astec plant, a natural gas-fired, 4 ton/batch plant, was tested in fulfillment of a condition written into its permit to construct and operate. The other plant, Tilcon, a 5 ton/batch plant, agreed to be tested at the request of the department. For testing purposes, Tilcon temporarily converted to its backup fuel, No. 2 oil. Connecticut has a wide variety of asphalt plants. The majority of Connecticut's 45 plants burn No. 2 oil with natural gas backup. The newer facilities are required to burn natural gas with No. 2 oil backup. The plants chosen for study were representative of typical facilities, both new and old. However, the study does require more testing of the older, oil-burning asphalt plants.

The concept for the project was formulated after attempts to estimate PAH emissions from asphalt plants for enforcement purposes were largely unsuccessful. Previously, estimated emissions of PAH or polycyclic organic matter (POM) from asphalt plants were based on limited non-specified test data. In addition, CT's existing hazardous air pollutant regulation for PAH was unclear and difficult to enforce because it was defined as PAH (benzene soluble). As an interim policy designed to facilitate the permitting of new asphalt plants, provisions were included in new permits to require testing for PAHs consequent to the development of an appropriate test method. As a result of this study, CT DEP now regulates specific PAH compounds and can specify a particular test method.

## EXPERIMENTAL METHODS

### Sample Collection

Two of the facilities CT DEP tested were at the Balf Company of Newington, which operates both batch and express or drum mix asphalt plants. The batch plant has a maximum operating capacity of 10 tons/batch while burning natural gas. The asphalt express process is a Gencor-Bituma drum mix asphalt plant. This plant has a maximum operating capacity of 450 tons/hour while burning natural gas. Both operations utilize a baghouse for particulate removal.

The PAH/NHC emissions from the plants were sampled in triplicate according to SW 846 Method 0010. The volumetric flowrate, moisture content, and stack gas composition were determined during each test run. All testing was performed on the exhaust stack. In conjunction with PAH/NHC testing, EPA Methods 1 through 4 were performed.

The PAH/NHC sampling method used the modified Method 5 sampling train. A modification in the sample recovery procedure was used and consisted of replacing the 1:1 mixture of methanol/methylene chloride rinse with separate rinses of acetone and methylene chloride. An acetone rinse followed by a methylene chloride rinse has been shown to be more efficient than the methanol/methylene chloride (1:1 volume) rinse. The PAH/NHC sampling method also included several unique preparation steps which ensured that the sampling train components were not contaminated with organics that may have interfered with analyses.

Triangle Laboratories, Inc. (TLI), Research Triangle Park, North Carolina performed the preparation of the glass fiber filters and the XAD-2 resin. All filters were cleaned before their initial use. The methylene chloride extract from the filter cleaning procedures was analyzed for PAH/NHCs. If any PAH/NHC was present in the concentration above the minimum detectable limit, the cleaning procedure was repeated and the extract reanalyzed until no PAH/NHC was detected.

The XAD-2 resin was placed in a soxhlet and extracted with HPLC grade water, methanol, and methylene chloride. After extraction, the resin was dried and placed in the sampling cartridges which were tightly capped with glass plugs. The extracts were then analyzed for total chromatographic organics (TCO) and targeted PAH/NHC compounds. If any PAH/NHC were present at a concentration above the minimum detectable limit and/or the TCO was greater than 20 ug/ml, the cleaning procedure was repeated until each criteria was met. In addition, the resin of each trap was fortified with 100 pg/ml of d14-Terphenyl<sup>2</sup>.

### Sample Analysis

High resolution gas chromatography/high resolution mass spectroscopy (HRGC/HRMS) analytical methodology was developed by TLI to satisfy CT DEP's monitoring objectives <sup>3</sup>. These objectives included determining the analytical feasibility of monitoring for 29 polynuclear aromatic hydrocarbons and five nitrogen heterocycles in asphalt plant stack samples. These compounds are listed in Table 1.

Table 1.  
List of Target Polycyclic Aromatic Hydrocarbons  
and Nitrogen Heterocycles.

Naphthalene	2-Methylnaphthalene	Acenaphthene
2-Chloronaphthalene	Acenaphthalene	Fluorene
Phenanthrene	Anthracene	Carbazole
Acridine	Fluoranthene	Pyrene
3-Methyl-fluoranthene	Cyclopenta-c,d-pyrene	Benzo-a-anthracene
Chrysene	Perylene	Benzo-b-fluoranthene
Benzo-j-fluoranthene	Benzo-k-fluoranthene	Benzo-a-pyrene
Benzo-e-pyrene	7H-Dibenzo-c,g-carbazole	Benzo-[ghi]-perylene
Dibenz-[ah]-anthracene	Dibenz-[aj]-anthracene	Dibenz-[aj]acridine
Dibenz-[ac]-anthracene	Dibenz-[ah]-pyrene	Dibenz-[ai]-pyrene
Dibenz-[ae]-pyrene	Dibenz-[al]-pyrene	Indeno-[1,2,3-cd]-pyrene
7,9-Di-Methyl-benz-c-acridine		

No problems were noted by TLI's sample preparation and mass spectrometry groups while performing the analyses. However, several factors did impact data validity. One of the factors was matrix related interferences which affected the quantitation of some analytes. This problem was described as severe in some samples. Quantitation of naphthalene, chloronaphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, acridine and carbazole could not be performed in a particular sample as a result of the matrix interference. TLI did provide quantitative results for these analytes in that sample which were believed to be minimum estimates. However, these values were not reliable enough to support an enforcement action. High recoveries of some internal standards were calculated in samples as a result of this interference. TLI modified their cleanup procedures in an attempt to more effectively remove the matrix interferences.

A second factor was that the results of all samples displayed selective losses during extraction for the labeled acridine and carbazole internal standards. Since the associated analytes act chemically in the same fashion, it can be assumed that these and other nitrogen heterocycles are selectively lost during extraction.

Another factor was that "b" and "j" isomers of benzofluoranthene as well as the "ac" and "ah" isomers of dibenzoanthracene coelute. Therefore, quantitative results were provided as a total for each isomer pair.

The last factor of concern was that saturated peaks (i.e. beyond calibration) were noted in all the samples. TLI believed that quantitative results for saturated signals were "minimum estimates".

The total PAH concentration was calculated for each sample. Naphthalene, 2-methylnaphthalene, and 3-methylfluoranthene were not included in the total PAH concentrations.

## RESULTS

CT DEP reviewed data from both oil and natural gas-fired batch operations as well as batch and express plant operations. Table 2 lists the comparison of data from asphalt batch and express processing plants firing natural gas. Table 3 shows a comparison of three asphalt batch plants. The Balf and Astec plants were firing natural gas. The Tilcon plant was firing No. 2 oil.

Table 2.  
Natural Gas-Fired Asphalt Batch and Express Plants  
PAH Data Excluding Naphthalene (ug/m<sup>3</sup>).

<u>Analyte</u>	<u>BATCH</u>	<u>EXPRESS</u>
Acenaphthene	1.75 (27%)	0.364 (9.4%)
Acenaphthylene	0.25 (4%)	1.185 (31%)
Fluorene	2.28 (36%)	0.848 (22%)
Phenanthrene	1.88 (29%)	1.147 (30%)
Anthracene	0.06 (1%)	0.066 (1.7%)
Fluoranthene	0.05 (1%)	0.119 (3.1%)
Pyrene	0.07 (1%)	0.081 (2.1%)
Benzo-a-Anthracene	6.7E-4 (.01%)	0.003 (.08%)
Chrysene	0.01 (0.2%)	0.024 (0.6%)
Benzo-k-Fluoranthene	0 (0%)	0.002 (.04%)
Benzo-j-Fluoranthene	0 (0%)	0 (0%)
Benzo-b-Fluoranthene	0.0017 (.03%)	0.005 (.12%)
Benzo-e-Pyrene	0.005 (.08%)	0.008 (.21%)
Benzo-a-Pyrene	0.0007 (.01%)	0.003 (.08%)
Indeno-123-cd-Pyrene	0.0027 (.04%)	0.003 (.08%)
Benzo-ghi-Perylene	0.027 (.43%)	0.023 (0.6%)
Dibenzo-ah-Anthracene	0 (0%)	0 (0%)
<u>Total PAH</u>	<u>6.4</u>	<u>3.9</u>

## DISCUSSION

The majority of the observed PAH emissions were comprised of: acenaphthene (24%), acenaphthylene (10.7%), fluorene (34.3%), phenanthrene (22.6%), anthracene (2.7%), fluoranthene (2.4%), and pyrene (1.8%). These 7 PAHs make up approximately 98-99% of the PAHs identified in the stack effluent samples. Naphthalene, 2-methylnaphthalene, and 3-methylfluoranthene were not included.

Emissions from the No.2 fuel oil fired batch process appeared to be twice the emissions from the natural gas fired process. Emissions from the express drum mix plant appear to be 40% lower than the batch plant (both plants natural gas-fired). Although the data base was quite small, it appeared that acenaphthylene was significantly more prevalent in the express plant samples. Correspondingly, acenaphthene seemed to be far more predominant in the batch samples.

## CONCLUSIONS

### Regulatory Implications

The following analytes were dropped from the target list of PAH/NHC compounds: 2-chloronaphthalene, carbazole, acridine, cyclopenta-cd-pyrene, dibenz-aj-acridine, 7,9-dimethyl-benz-c-acridine, perylene, 7H-dibenzo-cg-carbazole, the "ac" and "aj" isomers of dibenzanthracene, and the "al", "ae", "ai", and "ah" isomers of dibenzpyrene. These compounds were seldom if at all detected and then, only at trace levels in samples which contained relatively high PAH levels (especially when compared to ambient concentrations).

Table 3

Asphalt Batch Plants PAH Data Excluding Naphthalene (ug/m<sup>3</sup>).

<u>Analyte</u>	<u>BALF</u>		<u>ASTEC</u>		<u>TILCON</u>	
	Natural Gas-Fired 10 ton/batch		Natural Gas-Fired 4 ton/batch		No. 2 Oil-Fired 5 ton/batch	
Acenaphthene	1.75	(27%)	1.46	(22.5%)	3.12	(28%)
Acenaphthylene	0.25	(4%)	1.19	(18.3%)	0.37	(3.3%)
Fluorene	2.28	(36%)	1.26	(19.4%)	5.18	(47%)
Phenanthrene	1.88	(29%)	2.2	(33.8%)	1.09	(9.8%)
Anthracene	0.06	(1%)	0.032	(.5%)	0.6	(5.4%)
Fluoranthene	0.05	(1%)	0.133	(2%)	0.36	(3.2%)
Pyrene	0.07	(1%)	0.117	(1.8%)	0.23	(2.1%)
Benzo-a-Anthracene	6.7E-4	(.01%)	0.004	(.06%)	0.016	(0.14%)
Chrysene	0.01	(0.2%)	0.015	(.23%)	0.086	(0.77%)
Benzo-k-Fluoranthene	0	(0%)	0.003	(.05%)	6.7E-4	(.006%)
Benzo-j-Fluoranthene	0	(0%)	-	-	0	(0%)
Benzo-b-Fluoranthene	0.0017	(.03%)	0.013	(0.2%)	0.006	(0.05%)
Benzo-e-Pyrene	0.005	(.08%)	0.006	(.09%)	0.008	(0.07%)
Benzo-a-Pyrene	0.0007	(.01%)	0.0019	(.03%)	6.7E-4	(.006%)
Indeno-123-cd-pyrene	0.0027	(.04%)	0.003	(.05%)	0.006	(0.05%)
Benzo-ghi-Perylene	0.027	(.43%)	0.058	(0.9%)	0.044	(0.4%)
Dibenzo-ah-Anthracene	0	(0%)	0.0014	(.02%)	0	(0%)
<u>Total PAH</u>	<u>6.4</u>		<u>6.5</u>		<u>11.1</u>	

CT DEP now requires SW846 0010 as the PAH test method. Acetone and methylene chloride are to be used as the sample recovery solvents. Analysis is performed with HRGC/HRMS. Monitoring for nitrogen heterocycles requires additional method development and validation as well as separate sampling and analyses from PAHs. Therefore, CT DEP is not requiring sources to test for NHCs.

The asphalt plants fired with natural gas were generally well below CT DEP's maximum allowable stack concentration for PAH. The plant fired with No. 2 fuel oil was approximately 5 times the allowable stack concentration.

CT DEP has developed a proposed regulation for PAH and naphthalene as a result of this project. The ambiguity of the existing definition and multiple listings of PAH compounds in the regulations hampered both the CT DEP and the sources in determining compliance and performing appropriate monitoring.

CT DEP proposed the following definition be added to the regulations: (PAH) will be defined as the sum of the following compounds: acenaphthene, acenaphthylene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(k)fluoranthene, benzo(j)fluoranthene, benzo(b)fluoranthene, benzo(e)pyrene, benzo(a)pyrene, indeno-1,2,3-cd-pyrene, benzo-ghi-perylene, dibenzo-ah-anthracene.

CT DEP proposed the following items be deleted from the existing regulations: benz(a)pyrene, coal tar pitch volatiles, polynuclear aromatic hydrocarbons (PAH), benz(a)anthracene, benzo(b)fluoranthene, chrysene, 7H-dibenzo(c,g)carbazole, dibenzo(a,h)anthracene, dibenzo(a,h)pyrene, dibenzo(a,i)pyrene, indeno(1,2,3-cd)pyrene, and, asphalt (petroleum) fumes. CT DEP also proposed to redefine "naphthalene" as the sum of both naphthalene and 2-methylnaphthalene.

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## ESTIMATES OF PESTICIDE EXPOSURE FROM THE AGRICULTURAL HEALTH STUDY (AHS)

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### ABSTRACT

Several routes of pesticide exposure to farmer applicators were measured and compared. Whole body (WB) exposure was measured using  $\alpha$ -cellulose patches placed on the outer clothing of the farmer; two measures of hand exposures were taken, one using cotton gloves (GL) and the other using isopropanol handwipes (HA). Inhalation exposures were measured using a PUF cartridge coupled with a personal sampling pump. The three highest exposures received in descending order were: WB > GL > HA.

### INTRODUCTION

The primary goal of the Agricultural Health Study (AHS) sampling program is to provide quantitative measures of pesticide exposure from different farm tasks. In this study, the term exposure is defined as what contacts a person, whether on clothing, skin, or through simple processing by breathing or ingestion. Absorption and metabolism after this contact takes place is not considered here.

### METHODS

All of the methods for collecting the field samples used to assess exposures to pesticides can be found in Harding et al.<sup>1</sup> The analytical methodology used to analyze all field samples can be found in Geno et al.<sup>2</sup>

### RESULTS AND DISCUSSION

#### Hygiene, Activity Patterns and Demographics

**Hygiene.** The degree that each farmer practiced good hygiene varied substantially from farm to farm. Farmers 2 and 3 exercised more caution while loading and mixing pesticides. Farmer 2 was the most careful in the use and application of his pesticides. He did not experience any spills or splashes during loading and mixing of the pesticides. When applying the pesticide to his crop, he was inside an enclosed cab. A drift retardant was added to the pesticide application mixture. Farmer 2 also tried to purchase only that amount of pesticide needed for a specific job reducing leftover waste. He did have to stop work to make a five-minute repair on a leaking hose. He wore approximately the same clothing as the other farmers. This included a baseball cap, cotton gloves, a cotton work shirt and pants, and shoes. Farmer 2 washed his hands within 15 minutes after leaving work.

Farmer 3 also exercised good care in handling of pesticides. He wore rubber or leather gloves during all phases of his work. While applying pesticides, he had to stop work for approximately two minutes to repair a nozzle. This farmer also did spraying of hogs inside a barn with an aerosol can. He washed his hands within 30 minutes after leaving work. Farmer 3 was observed eating his lunch in the field, during a work break, without first washing his hands.

Farmer 1A also may have contaminated himself while hosing down some hogs with lindane. Farmer 1A does animal application of pesticides four times yearly. He washed his hands within one to two hours after leaving work.

Farmer 1B poked a hole through a container of alachlor and saturated the finger of one of the cotton gloves he was wearing. This glove was removed because of the chance of high exposure. Otherwise, Farmer 1B reported little hand contact with any pesticides, since he reported that he washed his hands between each loading. Farmer 1B also applied pesticides to animals six times yearly.

All the farmers changed clothes once a day, and their work clothes were washed once every three days.

**Activity Patterns.** All the farmers spend as much as 16 hours in the field during a busy season. Crops can be sprayed every day for up to a two-week period. Farmer 1A reported being active during work and inactive during leisure hours. Farmer 1A had a three year old child. This child's activities were reported for a total period of 70 hours. Out of this total time of 70 hours only one and one-half hours were spent playing in dirt by the child. No hand-to-mouth activity was reported although some probably occurred. While not working, Farmer 1B spent most of his time with his spouse indoors during the monitoring period. The family of Farmer 2 all participated in planting and gardening. The wife of Farmer 2 spent four and one-half hours in the field during the three-day monitoring period. She spent three and one-half hours of this time in the field while pesticides were being applied. The family of Farmer 3 also participated to varying extents in lawn and gardening activities.

**Demographics.** At Farm 1A there was a married couple between the ages of 26 to 45 years old. They had two children, a son approximately one year old and a daughter three years old. Farmer 1B and his spouse were at least 60 years old. Farmer 2 and his spouse were 26 to 45 years of age. They had a 15 year old son and a 13 year old daughter. Farmer 3 and his spouse were 26 to 45 years old and had a daughter eight years old and a son four years old.

#### Occupational Exposure of Farmers During Monitoring Events

**Hand Versus Inhalation Exposure.** The highest (but not the only) exposures to the hands can occur during accidental spills and splashes, while loading or mixing pesticide, or during repairs on leaky hoses or nozzles. An accidental spill with cotton glove and possible hand contamination did occur on Farm 1B on Day 4 of the monitoring period. This accidental spill at this farm highlights the importance of considering hand exposure. Also, it is unknown whether any of the farmers, while at work, washed their hands before urinating. If not, some pesticide may have been transferred from the hands to the genital area. This is of special concern because of the thin dermal layer of the penis and scrotum through which pesticides will transfer readily.

Table I addresses two issues. One concerns the inhalation exposure (BC, see Table I) received by the farmer during monitored application events. The second is the comparison of total exposure in milligrams received by the hands (HA, see Table I) as compared to the total milligrams sampled in the farmer's breathing zone. It is clear that for those cases for which a TLV (Threshold Limit Value) was available, the farmers' inhalation exposures, while working during the monitoring periods, were far below the TLVs.<sup>3</sup> A similar comparison can be made between the mass of pesticide recovered from the hands and the mass collected by personal air sampling. The mass of pesticide measured on the hands is far greater than that collected by personal air sampling.

Table I. Comparison of handwipe amount to breathing concentration and amount inhaled.

Farm by Event <sup>(1)</sup>	Time (h)	TLV (mg/m <sup>3</sup> )	BC <sup>(2)</sup> (mg/m <sup>3</sup> )	HA <sup>(3)</sup> (mg)	Mass Processed by Inhalation During Work (mg) <sup>(4)</sup>
<b>Alachlor</b>					
1B-3A	3.000	NONE	0.008	6.380	0.043
1B-3B	5.400	NONE	0.011	14.800	0.110
1A-3C	2.600	NONE	0.014	0.480	0.065
1B-4A	3.300	NONE	0.020	9.540	0.120
<b>Atrazine</b>					
1B-3A	3.000	5	0.002	2.000	0.011
1B-3B	5.400	5	0.002	4.330	0.019
1A-3C	2.600	5	0.003	0.113	0.014
1B-4A	3.300	5	0.003	3.76	0.018
<b>2,4-D Isooctyl Ester</b>					

2-3	3.000	NONE	0.001	0.152	0.005
Lindane					
1A-4B	1.100	0.5 (SKIN)	0.001	0.152	0.010
Pyrethrins					
3-4A	0.045	5	0.240	0.450	0.020
Trifluralin					
2-3	3.000	NONE	0.001	0.023	0.005

- (1) All pesticides applied during these events. See Table IV for explanation of coded events.
  - (2) BC = The average breathing concentration (mg/m<sup>3</sup>) during the application of pesticides.
  - (3) For the HA (applicator handwipe) data, recovery from the skin is unknown. Recovery from the isopropyl-saturated cotton gauze used to take the handwipes was good. Biases in the HA data due to skin absorption or other mechanisms is unknown.
  - (4) Calculated by multiplying time (h) \* BC (mg/m<sup>3</sup>) \* 1.8 m<sup>3</sup>/h (see note below).
- TLV Threshold Limit Value (mg/m<sup>3</sup>), defined as that concentration in air that a healthy worker may be exposed to for an eight-hour working period presumably without adverse health effects resulting.

NOTE: A moderate workload was assumed for the farmers with a breathing rate of 1.8 m<sup>3</sup>/h. The personal air samplers were run at 0.23 m<sup>3</sup>/h.

Inhalation exposure is most likely to occur from overspray while the pesticide is being applied to the crops. Some small contribution may be received during mixing and loading.

**Whole Body Exposure Versus Hand.** Another measure of integrated exposure is whole body (WB) exposure. This was calculated using a scaling factor for each farmer. This scaling factor was calculated by first obtaining the surface areas of the farmers' bodies off a nomogram.<sup>4</sup> This required a knowledge of each farmer's height and weight. Next, the total area of the analyzed body  $\alpha$ -cellulose patches was calculated. Then to get the scaling factor the estimated surface area of the farmer was divided by the total area for all three analyzed body  $\alpha$ -cellulose patches. The results of these calculations are in Table II. To calculate the estimated whole body (WB) exposure, the corresponding body patch concentration was multiplied by the scaling factor to yield a result in milligrams. These results were then compared to the measured mass in milligrams on the cotton gloves as is shown in Table II. Comparing the median values in Table II shows that the estimated WB > GL, but on the same order of magnitude.

Table II. Comparison of whole body exposure to pesticide retained on cotton gloves.

Farm by Event*	DP (mg)	Scaling Factor	Whole Body Exposure (WB in mg)	GL (mg)
Alachlor				
1B-3A	2.05	223	457	105
1B-3B	5.39	223	1022	270
1A-3C	0.38	218	83	59.8
1B-4A	1.02	223	227	>2370 <sup>(1)</sup>
Atrazine				
1B-3A	0.137	223	30	2.37
1B-3B	0.296	223	66	33.2
1A-3C	0.114	218	25	5.25
1B-4A	0.373	223	83	16

Table II. Comparison of whole body exposure to pesticide retained on cotton gloves.

Farm by Event*	DP (mg)	Scaling Factor	Whole Body Exposure (WB in mg)	GL (mg)
2,4-D Isooctyl Ester				
2-3	0.00891	202	1.8	29.3
Lindane				
1A-4B	0.375	218	82	21.2
Pyrethrins				
3-4A	0.023	202	5	2.53
Trifluralin				
2-3	0.00047	202	<u>0.1</u>	<u>0.252</u>
			MIN=0.1	0.252
			MAX=1078	2370
			MEDIAN=67	25.25

\* All pesticides applied during these events.

(1) Finger tip of glove saturated with pesticide.

DP Dermal  $\alpha$ -cellulose patches attached to front of thighs and to the back of the nape of the neck.

SCALING FACTOR: Estimated surface area of farmer divided by total area of all three body  $\alpha$ -cellulose patches.

WB Whole body exposure (mg).  $WB (mg) = (DP) * (SCALING)$ .

GL Cotton glove measurements (mg).

**Application Versus Nonapplication Events.** Day 2 at all farms and Day 4 at Farm 2 were baseline days during which no pesticides were applied to the crops. Days 3 and 4 were days during which pesticides were applied to the crops. It is useful to compare the exposures received by the farmers on Day 2 to those received on Days 3 and 4.

It has been shown above that handwipe (HA) data are a good measure of the farmer applicator's exposure. A comparison of application day exposure versus baseline day exposure is given in Table III for the applicator handwipe data. Note that the summary statistics in Table III represents all detected handwipe measurements of all analytes grouped together, separately for application and nonapplication days. The median value for all the measurements taken on application days is four orders of magnitude above baseline days. The maximum for Days 3 and 4 is also much greater than that for Day 2. This indicates an increase in exposure due to pesticide handling and application.

Table III. Farmer handwipe exposure (mg) on application versus nonapplication days.

Percentiles for Nonapplication Days				
10%	25%	50%	75%	100%
0.000015	0.000045	0.000085	0.0029	0.530

N=35

MIN=0.000015

MAX=0.530

MEDIAN=0.000085

**Percentiles for Application Days**

10%	25%	50%	75%	100%
0.00044	0.0162	0.160	3.76	14.80
N = 18				
MIN = 0.00044				
MAX = 14.80				
MEDIAN = 0.16				

**CONCLUSIONS AND RECOMMENDATIONS**

The three highest exposures received in descending order were: WB > GL > HA. The exposure to the whole body (WB) was comparable to the cotton glove (GL) data. Both represent an integrated average over the work period. WB exposure is an estimated value which assumes the sampled dermal patch areas are representative of exposures received by all body surfaces. GL exposure is calculated from direct measurements. Because WB exposure is an estimated value, this tends to lessen the confidence in the results. GL data may be superior to WB estimated values, but there were problems with the collection of the GL data. The cotton gloves either were poor fitting or restricted the farmer in his ability to do his job effectively.

Greater care in exercising good hygiene practices could substantially reduce the farmer applicator's exposure as well as that of their families. Such practices could include: cautious handling of pesticides, developing proper hand washing habits, removing shoes prior to entering the home, bathing immediately after work, and washing work clothes separately in cold water.

Table IV. Event ID code.

Farm ID	Week Monitored	Sampling Period/Event
1A	Week 1	2 Day 2
1B	Week 1	3 Day 3
2	Week 2	3A - Day 3, 1st event/sample
3	Week 3	3B - Day 3, 2nd event/sample
		4 Day 4
		4A - Day 4, 1st event/sample
		4B - Day 4, 2nd event/sample

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