

Measurement of Toxic and Related Air Pollutants

**May 7-9, 1996
Sheraton Imperial Hotel
Research Triangle Park, North Carolina**

A Symposium Sponsored by:

Air & Waste Management Association



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ABSTRACTS

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and
U.S. Environmental Protection Agency**



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and Robert G. Fuerst, U.S. EPA, Research Triangle Park, NC*

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Session 1

Semivolatiles

Chair: Joachim D. Pleil, U.S EPA, Research Triangle Park, NC

Comparison of On-line and Off-Line SFE GC/MS Methods for the Determination of SVOCs from Tenax-GC Filled Cartridges

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Supercritical fluid extraction (SFE) has become the main alternative to Soxhlet extraction of analytes from environmental samples primarily because of the shorter turnaround time in analysis, reduced solvent exposure and disposal problems, and comparable extraction efficiencies. SFE has been shown to be comparable to Soxhlet extraction for extracting analytes from a variety of substances including carpet, soils, and air sampling sorbents. The objective of this study was to compare two means of introducing SFE extracts, taken from 1-mL Tenax-filled stainless steel cartridges, to a GC/MS interface and an off-line SFE GC/MS system for determination of semivolatile organic compounds (SVOCs) as both spiked samples and ambient air samples. Ambient air samples were obtained by using a 6 L canister as a vacuum source, thereby collecting a given volume of sample in a very simple and easily transportable manner. Results indicated that the methods were equally good at extracting various compounds from the cartridges, but the on-line method had better recovery for the more volatile SVOCs. Other advantages for the on-line method included less sample handling and indications of lower limits of detection than the off-line method.

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Phase Distribution of Formic Acid

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Formic acid is produced in the aqueous-phase of the atmosphere, in part,

through the photo-oxidation of formaldehyde by hydroxyl radicals. One of the products of this photoreaction is the formate anion. As acidic hydrometeors such as fog, dew droplets, and clouds evaporate, the formate anions can recombine with hydrogen ions to produce volatile formic acid. The dispersion of formic acid at the aqueous/gas interface is controlled by the reverse deposition rate measured in nanomoles/cm²/min.

Experiments are performed to measure the reverse deposition rate of formic acid produced by the air drying of acidified aqueous solutions of formate anion. Ultra pure air, maintained at constant temperature and relative humidity, flows over the liquid surface of acidified formate droplets for varying periods of time. The solutions are contained in U-shaped FEP Teflon tubes which measure 23 centimeters in length and 1.3 centimeters in diameter. The tubes are connected to a series of two glass bubblers containing 0.01 N NaOH. Ion Chromatography (IC) is used to determine the loss of formate anion occurring in the droplets. Formic acid is measured by analyzing the formate concentration of the 0.01 N NaOH solution at the conclusion of each experiment. The analytical results are used to calculate the amount of formate contained in the applied formate solution, the droplet residue, and in both bubblers.

Phase Distribution of PAH Under Different Atmospheric Conditions

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The vapour/particle phase distribution and particle size of airborne PAH are important for determination of the potential health hazard posed by exposure to the PAH. The behaviour of 12 PAH in a dynamic, controlled test atmosphere produced by dispersion of fortified woodsmoke particles (> 80 % of mass median diameter < 3.3 μ m) in a special apparatus was examined at different conditions of temperature (6 - 32°C), relative humidity (23 - 71 %), and particle concentrations (140 - 1000 mg/m³). Seven different active sampling trains containing filters followed by porous polymer sorbents, and operated at different air sampling rates (0.7 - 33 L/min), as well as two types of passive samplers were used to collect the airborne vapour and particle phase PAH. The PAH were extracted, and the extracts were analyzed by GC-MS. Typically, less than 40% of naphthalene, fluorene and phenanthrene, and more than 90% of dibenzo(a,h)anthracene and benzo(g,h,i)perylene, was found on the filters. The influence of humidity, temperature, particle concentration, and sampling rate on the apparent phase distribution of the PAH, and the relationships between some of these parameters will be discussed.

Fine Particulate Nitro and N-Nitroso Organic Compounds in the Atmosphere

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Photochemistry between gas phase organic compounds, NO_x and ozone is expected to result in the formation of nitrogen oxide containing compounds of toxicological importance. Classes of compounds which may form include nitro and N-nitroso substituted organic compounds. Many of these compounds will be labile, semi-volatile organic compounds in equilibrium between the gas and particulate phases in the atmosphere. The phase distribution of these potentially toxic semi-volatile organic compounds may be determined using diffusion denuder sampling technology. The total concentration of N-nitroso compounds in the collected samples is determined using N-nitroso specific denitrosation reactions followed by detection of the NO with a TEA. Specific nitro and N-nitroso compounds are detected using supercritical fluid chromatography, SFC, coupled to the TEA using nitro- and nitroso-specific chemiluminescence detection. These analytical techniques for the sampling and determination of total N-nitroso material, and the separation and determination of specific N-nitroso and nitro compounds have been used for the characterization of these compounds in samples collected in Provo, Utah. The results indicate that the majority of the N-nitroso and nitro organic compounds present in fine particulate matter in the urban area studied are semi-volatile organic compounds which are easily lost from particles during sampling. Furthermore, the concentrations of these fine particulate compounds are comparable to the concentrations of gas phase nitro and N-nitroso organic species. Detailed analyses of nitrogen, nitro- and nitroso-organic semi-volatile compounds can be expected to improve our understanding of the etiology of observed health effects associated with exposure to ambient fine particles.

Session 2

VOC

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New York State Department of Environmental Conservation PAMS Monitoring System Using A 3-Column, Double Identification GC

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New York State conducted its 1995 PAMS measurements for New York City in the Bronx (New York Botanical Gardens) using a Perkin-Elmer ATD-400 Thermal Desorption Unit with an 8000 Series Gas Chromatograph. Data was collected in New York City, transferred to Albany, and processed in the central office. The system was checked on a daily basis from Albany to verify operation. Quality assurance for the system was provided by collecting a one hour collocated canister sample every day with analysis performed in Albany using a GC-MS system. The normal configuration for the Perkin-Elmer system uses only two columns, a Plot column to separate low weight hydrocarbons (C2-C5) and a BP-1 column to separate higher weight hydrocarbons (C6-C10). New York's custom designed system uses a third RTX-5 column to provide a second identification and quantitation of most target hydrocarbons. Analysis of the 1995 data provides insight into the usefulness of the third column in correcting both misidentified peaks and over-quantification of compound concentrations found using the standard configuration alone. The 1995 data set also allows an examination of the increased complexity versus the benefits of the system modification.

Portative Device for Long Term Integrative Personal Sampling of VOCs and Other Gaseous Air Pollutants

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Apart from passive dosimeters based on the principles of diffusion on sorbent materials, VOCs can be collected passively using evacuated sampling vessels such as SUMMA canisters. The basis of this last methodology was never

applied for personal sampling because of physical limitations in size and flow controlling capacities. From the development of an innovative mechanical controller which can extend the sampling duration and can theoretically achieve any flow rate, we have recently designed a portative device for passive personal monitoring of VOCs and others gaseous air pollutants such as CO, CO₂ or CH₄. Prototypes were assembled and tested in the laboratory. They were made with a rectangular stainless steel vessel of 150 ml equipped with a pressure gauge and a valve, and connected to our novel flow controller. For industrial hygiene applications, sampling time was defined at 40 hours. The personal sampler was able to maintain a constant flow rate during 5 consecutive periods of 8 hours over one week. To verify the integrity of long term passive samples using this portative device, prototypes were challenged with a 100 ppb(v) gas mixture of 40 air toxics. Analysis was performed on a GC/MS using sorbent concentration and drypurge techniques where 10 ml of samples were withdrawn from the vessels with a gas tight syringe and injected into the system. Results demonstrated the reliability of the personal passive portative device and its applicability for workplace monitoring. Compare to passive sorbent badges, the performance of this new device is less affected by temperature and by humidity. The portative passive monitor can be applied to sample workers or commuters in outdoor and/or indoor environments. Considering the possibilities offered by the flow controller which is the key part of the device, sampling time can be adapted for any situations and mean exposure can be more easily obtained for the benefit of air quality studies.

A New Method for Measuring Vapor Emissions

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A new approach for measuring point-source emissions of volatile organic compounds, acidic vapors, and other species is presented. The basic principle is that the amount emitted is determined directly, by mass, and is cumulative rather than intermittent. As a result, wide fluctuations of concentration and erratic flow behavior are accommodated without affecting the accuracy of the measured emission rate. The vapors are retained by a sorbent, such as activated carbon, ion exchange resin, or zeolite, or a combination of those.

Validation tests have been conducted in which a known quantity of vapor in a carrier gas was admitted to the test unit, and that was compared with the amount measured. The vapor comprised a single VOC, a mixture of VOCs, or a mixture of a VOC with water. Conditions studied were: the compound or mixture of compounds, concentration, carrier gas, flow rate, and adsorbent. In some tests the VOC was admitted intermittently. The VOCs included: hexane, acetone, toluene, vinyl acetate, and 1,1,1 trichloroethane. The average absolute error of

the delivered and measured VOC emission rates was 6.8% and the standard deviation was 3.4%.

Overview of Prototype EPA PAMS Data Analysis Workshop

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In December 1995, the EPA sponsored a prototype PAMS data analysis workshop. The objectives of this workshop were to present, explain, and discuss various methods, procedures, and tools for use in analyzing PAMS and similar aerometric data; to provide a forum for nationwide communication and information transfer on the analysis of PAMS data (and that of supplemental air quality monitoring campaigns and/or field studies); to assist state and local agencies in the use of these methods, procedures, and tools in the analysis of PAMS and similar data sets; and to contribute to the general body of knowledge and literature on air quality analysis through demonstration of case studies and examples. The topics discussed in the workshop included: data validation, VOC spatial and temporal issues, ozone accumulation potential, biogenic emissions, use of indicators to assess NO_x and VOC limitations, comparisons of UAM results with ambient data, emission inventory evaluations, receptor modeling, trends analyses, 3-D analyses, and case studies. This paper will provide an overview of the workshop and provide key examples of featured topics.

Endocrine Disruptor Exposure Research

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Scientists continue to enhance techniques to estimate exposure of human populations and ecosystems to environmental contaminants. The U.S. Environmental Protection Agency's scientists are studying the exposure of humans and ecosystems to chemical substances that are persistent, can bioaccumulate, and can biomagnify in the food chain. A growing number of studies suggest that several persistent organic pollutants (POPs) and some organic forms of heavy metals appear to mimic or to disrupt hormonal mechanisms in humans and wildlife. EPA is exploring methods and models to measure and to predict exposure to these substances. The presentation will address some of the approaches the Agency may take to conduct exposure research of endocrine disrupting compounds within the Agency's risk assessment framework. Persistent organics, such as those listed recently by the Inter-Organizational Program

for the Sound Management of Chemicals, should be characterized physically and chemically to estimate bioavailability and their potential for endocrine effects. Models will need to be developed to estimate the chemical forms, atmospheric and hydrological transformations after release to the environment, and the fate of these substances within environmental media and the food chain.

Data Validation of PAMS Auto-GC VOC Data: Lessons Learned

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We have performed data validation of continuous VOC data collected with automated GC systems as a part of the PAMS network in Connecticut. Using a graphical platform from which to display the data, we performed quality control tasks on the data and began data analyses. The hourly concentrations of the PAMS target species were displayed in several ways including scatter plots, "fingerprints", and time series. Using scatter plots, we investigated the relationship between species at one site or at a pair of sites. Fingerprint plots show the concentration of each species in a sample (in roughly chromatographic order) and help to identify unique characteristics of the samples. Time series plots show the concentrations of species in every sample over a specified time period and are useful in showing the diurnal behavior of a species. The retention times of the species (rather than the concentrations) were also explored using the same graphical features. Calibration data, contamination from shelter off-gassing, cold trap failure, and other problems were identified. We will discuss and provide examples of our findings; these results will aid others in evaluating their continuous VOC data.

Analysis of VOC Data in Support of Pollutant Transport Studies in Shasta County, California

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The Shasta County Air Pollution Control District has funded a study to investigate the origin and extent of ozone and ozone precursor concentrations that are due to upwind transport. As a part of the study, air quality measurements were made aloft during September 1995. Hydrocarbon measurements were made aloft for use as tracers of opportunity for analyzing the source of the air mass. Total nonmethane hydrocarbon, speciated hydrocarbons, and Aexotics@ including Freon 12, Freon 11, Freon 113, chloroform, 1,1,1-trichloroethane, carbon tetrachloride, trichlorethylene, and perchloroethylene were quantified. In earlier studies of transport in this region, a hydrocarbon and exotic species signature for the Sacramento metropolitan area was identified. This signature will be compared to the signatures developed from samples collected in Shasta County to determine evidence of transport. The relative age of air parcels entering the area will also be determined using the ratios of more reactive species to less reactive species concentrations; lower ratios correspond to more aged hydrocarbon mixtures. This paper will discuss the analyses of the hydrocarbon and exotics data and the implications of the results to transport in the region.

VOCs from Marker Pens in Exposure Scenarios

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Human exposure to volatile organic compound (VOC) vapors emitted by several types of marker pens, both indelible and erasable, was studied experimentally and by modeling. VOCs emitted by the pens were identified by gas chromatography-mass spectrometry, and airborne VOC concentrations were measured both in a room-size controlled-environment chamber, and in an actual classroom. A variety of VOCs including alcohols, methyl isobutyl ketone, the isomeric xylenes, and ethylbenzene, were emitted by different types and brands of pens.

In the chamber, vapor concentrations in the user's breathing zone were higher than those near the chamber corner. The concentration profiles were fitted to an indoor air quality model which allowed estimation of VOC emission rates. The model accounts for the observed elevated concentrations in close proximity to the source and for adsorption-desorption "sink" effects. Model parameter values which fit the chamber data were subsequently used to model the data from a classroom. The results show that with the use of appropriate parameter values, indoor concentrations of vapors from this source type can be adequately simu-

lated with the proposed model. VOC exposure concentrations for relatively prolonged usage of some marker pens can be at the ppm level.

Emission of VOCs and Polynuclear Aromatic Compounds from Asphalts and Road Paving Operations

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Assessment of air pollutants from fugitive and new sources is crucial for cities and metropolitan areas such as Los Angeles that do not meet Federal air quality standards. Assessment of unknown sources or ones that have not been fully characterized for their contribution to background emissions is essential if reduction is sought. The South Coast Air Quality Management District (SCAQMD) initiated a study for the characterization, quantification and assessment of organic pollutants emitted from hot-mix asphalt manufacturing and road paving operations. The objectives of the study were to evaluate and quantify the magnitudes of these emissions as well as their contribution to smog in Los Angeles through photochemical transformation. This study which was partially supported by the National Science Foundation (NSF) and the Strategic Highway Research Program (SHRP) investigated several asphalts and bitumen for their emissions through extensive laboratory testing and field sampling programs. In order to be able to conduct these programs, a protocol for the sampling and analysis of these emissions had to be developed due to the complex nature of organic constituents in the emission matrix. The first phase of these laboratory investigations focused on the qualitative assessment of emissions. The second phase of the laboratory studies was directed toward the quantitative assessment of polynuclear aromatic hydrocarbons (PAHs) and volatile organic compounds (VOCs). Furthermore, in the second phase of these investigations, a specially designed solar simulator/exposure cell was used to simulate road paving conditions such as temperature, solar radiation intensity, and humidity. Asphalt emissions were then quantified under a variety of atmospheric conditions. In the field sampling phase of the study, samplers were installed in asphalt hot-mix manufacturing plants to monitor the emissions at various locations. The major area of contribution in the plants was the loading zone where the asphalt was loaded onto trucks. The second area monitored involved fugitive emissions from trucks during transportation of asphalt to paving sites. The third area was the paving site on the road where the asphalt was delivered to the paving machine and laid on the road surface. The fourth operation monitored was the compaction of asphalt by steel rollers. Based on the field and laboratory studies, the magnitudes of emissions from asphalt paving operations were estimated.

Monitoring for VOCs In Air - Status Report

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Recent methods development efforts for volatile organic compounds in air have included:

1. The placement of one methods description TO-15 on the the AMTIC Bulletin Board maintained by the Office of Air Quality Planning and Standards and the preparation of two others, TO-16 and TO-17. TO-15 describes the use of a canister-based sampling procedure and a GC/MS analytical procedure to monitor VOCs. Method TO-16 concerns the use of FTIR-based open path monitoring and the Method TO-17 involves the use of solid adsorbents for sampling of VOCs.
2. The publication of several journal article publications in support of methods development for the North American Research Strategy for Tropospheric Ozone (NARSTO) and the Photochemical Assessment Monitoring Stations (PAMS) network. These publications show how to monitor VOCs with better sample integrity than in the past, particularly with respect to polar VOCs.
3. The publication of several journal articles on the use of open path monitoring of VOCs in fence-line monitoring applications using FTIR-based systems. Emphasis has been placed on understanding and treating the generation of background spectra.
4. Evaluation of a new automated gas chromatographic system as part of the NARSTO contribution to the 1995 Southern Oxidant Study (SOS) Nashville Field Study. Diurnal patterns showing hourly updates for several biogenic compounds were seen for the first time.

Comparison of Acetone Concentrations in Ambient Air Using EPA Methods TO-14 and TO-11

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The accurate measurement of polar compounds, such as acetone, in the ambient air has proven to be difficult. In particular, determining low atmospheric concentrations for these compounds using current sampling and analysis methods has proved quite challenging. A comparison of two accepted sampling methods for acetone is currently being performed from measurements taken at a long-term ambient air monitoring network. Samples were collected at five sites using both SUMMA polished stainless steel canisters analyzed by CG/MD (modified TO-14) and dinitrophenylhydrazine (DNPH) coated silica gel cartridges analyzed by

HPLC (modified TO-11). Over the last four years more than 1800 canister and sorbent samples have been collected. In this paper we will show a complete statistical analysis of the measurements techniques discussed, noting significant differences or similarities between the two measurement methods. Statistical analysis for method accuracy and precision at different concentration levels (several orders of magnitude variance in concentrations) will also be discussed. The large number of samples will allow a significant evaluation of both techniques.

Recent Advances in the Analysis of Oxygenated Hydrocarbons

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The historical and conventional method of hydrocarbon speciation has been to remove water with a Nafion® dryer or some other water management method before passing the air sample through a freeze-out loop or cryofocusing step to concentrate/enrich the analytes for subsequent chromatographic analysis. This approach is robust and easily automated. Removal of the water from a whole air sample prior to the concentration step is essential to prevent the freeze-up of the trap. This approach has been used for hundreds of thousands of analyses over the past 30 years. Unfortunately, these water removal procedures, while generally not affecting the quantitative measurement of the hydrocarbons, do attenuate the more water-soluble organic compounds. Measurements we have made over the years indicate a significant fraction of the VOC in suburban, rural and remote atmospheres are not measured using the conventional method. In these non-urban samples, compared to urban samples, an homologous series of C₆-C₁₀ aldehydes is present that constitutes from 10% to as much as 90% or more of the VOC mass. Accounting for all of the carbon during the processing of whole air samples being prepared to measure the radiocarbon (¹⁴C) abundance in atmospheric VOC is a crucial issue when determining the relative contribution of carbon from biogenic- vs. fossil-carbon sources.

Analysis of Available Ambient and Stationary Source VOC HAP Sampling Results to Verify Emission Rate Estimates for Sources in Nogales, Sonora, Mexico

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The Arizona Department of Environmental Quality (ADEQ) is currently funding a project to develop comprehensive hazardous air pollutant (HAP) emissions inventories for the cross-border communities of Nogales, Arizona and Nogales, Sonora, Mexico. Ambient VOC and PAH data were collected in downtown Nogales, Sonora in July 1994 by the ADEQ. This paper addresses the detailed analysis of the ambient HAP data performed by the project team. The ambient HAP data evaluation serves as a vital cross-check of the accuracy of the HAP emission estimates developed for each source type included in the HAP emissions inventory.

The data show that benzene, toluene, xylene, ethylbenzene (BTXE) and aldehydes are the dominant VOC HAPs in the ambient air. The quantity of BTXE in the ambient air, and ratio of these compounds to each other, implies that mobile sources are the principal source of BTXE in Nogales, Sonora. Significant levels of olefinic VOCs were also detected.

Ambient test data also indicate ethane, propane, butane, pentane are the predominant VOC species in the ambient air. Compressed gas cylinders are the probable source of these VOCs. Almost all residential and commercial cooking performed in Nogales, Sonora is done from compressed gas cylinders containing a mixture of propane (primarily) and butane. These cylinders are ubiquitous, and many are equipped with potentially leaky valves. VOC and VOC HAP test protocols are currently being developed by the Mexican Institute of Ecology for these cylinders and associated cooking ranges.

Periodic open burning of municipal solid waste (MSW) is performed at a site located on the border in Nogales, Sonora. Ambient VOC HAP data collected in July 1994 during both MSW burning periods and "no burn" periods is being evaluated to determine if the contribution of open burning to the ambient HAP burden can be estimated for both particulate and VOC HAPs from the ambient data.

A Study of "Holding Times" for Sulfur Compounds in Restek's SilcoCan Canisters

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A simple, cost-effective method for sampling and analysis of H_2S , COS, mercaptans, organo sulfide, and disulfides in whole air samples is described. This method involves sampling sulfur compounds in humidified ambient air using Restek's SilcoCan canisters followed by analysis on a modified gas chromatograph/ flame photometric detector (GC/FPD). The stability of sulfur compounds was investigated at four different concentrations for 120 hours. The results show excellent stability of sulfur compounds in SilcoCan canisters over the time period studied. It is inferred from this study that SilcoCan canisters are suitable for sampling all VOCs including sulfur compounds.

Measurements of Hydrocarbons and Reduced Sulfur Compounds Emitted from a Wastewater Treatment Pond

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A flux chamber was deployed on the water surface to monitor the emissions of hydrocarbons and reduced sulfur compounds from a wastewater treatment pond at a refinery site. Air samples were collected in Tedlar bags and analyzed on-site by means of a gas chromatograph/ flame ionization detector (GC/FID) for hydrocarbons and a gas chromatograph/ flame photometric detector (GC/FPD) for reduced sulfur compounds.

The standard deviations of the duplicate samples for hydrocarbons and for reduced sulfur compounds were better than 4% and 11%, respectively. The pond was monitored during the daytime and nighttime, under two different weather conditions where the daytime temperatures were about 22 C and 14 C. The results showed that the difference between day and night emissions of hydrocarbons and reduced sulfur compounds were greater during warm weather compared to those during cold weather.

Air samples were also collected with charcoal adsorbent tubes and analyzed by means of a gas chromatograph/ mass selective detector (GC/MSD) at the BOVAR Environmental (BE) laboratory to confirm the GC/FID hydrocarbon analyses. There was excellent agreement between hydrocarbons identified by GC/FID and GC/MSD.

Extractive FTIR Technology - Applications In Combustion Source Measurements

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In response to the 1990 Clean Air Act requirements, the Gas Research Institute (GRI) is investigating emissions from industry equipment including glycol dehydrators, internal combustion engines, boilers, heaters, and incinerators. To characterize emissions from internal combustion engines reliably and accurately, GRI developed and validated a method based on extractive Fourier Transform Infrared (FTIR) technology. This paper will describe the FTIR test protocol approved by U.S. Environmental Protection Agency, including a brief discussion on external combustion source (i.e., boiler/heater/incinerator) FTIR measurement experience. In addition, the approach used in reference spectra development and the associated challenges will be described.

Session 3

Natural Emission of Oxidant Precursors

*Cochairs: Viney P. Aneja, NC State University, Raleigh, NC;
and Bruce W. Gay, Jr., U.S. EPA, Research Triangle Park, NC*

Project NOVA (Natural emissions of Oxidant precursors: Validation of techniques and Assessment) Overview

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This project attempts to determine the surface exchange fluxes of the oxides of nitrogen using several independent methods. It will then compare the results from dynamic enclosure techniques to measurements using the micrometeorological methods. Eddy correlation measurements of the turbulent fluxes of NO, NO₂ (or NO_x), and of O₃ together with gradient measurements of the same species will enable the soil emission of NO_x (= NO + NO₂) and the effect flux of NO_x to the free atmosphere to be compared over a range of atmospheric and soil conditions. A comprehensive characterization of the soil chemistry and microbiology was undertaken. The results of this study will enable a characterization of the dynamic enclosure technique which will be used to survey nitrogen oxide emissions of selected soils throughout the southeast United States.

Natural Emissions of Oxidant Precursors: Validation Of Techniques and Assessment (Project NOVA 1995) - Site Characterization

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A major objective of Project NOVA 1995 is to intercompare surface exchange fluxes of N and other gaseous species using both soil enclosure and micrometeorological techniques. This presentation provides the results of an intensive site characterization necessary for completion of this objective. The research site (approximately 136 ha of continuous corn [*Zea Mays*]; width 1067 m, length - 1280 m) is located in Washington County in the Northeastern Lower Coastal Plain region of North Carolina. The site has a SW - NE orientation, allowing a level fetch of ≈ 1000 m over a continuous corn canopy. The level topography results in soils with seasonal high water tables. Agricultural soils are drained with a series of parallel ditches (1 m depth; 50 m apart) connected to a series of larger ditches which drain into primary canals. Three soil types are present at the research site: a Conaby muck, an Arapahoe fine sandy loam, and a Portsmouth fine sandy loam. Visual observations via soil pits, and chemical analyses, reveal that the soils differ primarily in organic matter content and thickness of a distinct black surface horizon (bulk density ≈ 1.3 gm cc⁻³). The corn crop used for the study was planted 12 April 1995. N application totaled 184 kg N ha⁻¹, with 9 kg N ha⁻¹ placed in the row as starter fertilizer, and 73 kg N ha⁻¹ broadcast as a 30% N solution (equal parts urea, ammonia, nitrate) added at planting. The remaining 102 kg N ha⁻¹, in the form of the 30% N solution, was applied as a concentrated band (2 cm in width) on the soil surface down the center of the interrow on 20 May, 1995. Soil samples (0 - 30 cm depth, 10 cm increments) were taken daily to estimate soil water content and extractable N (IN KCl; NH₄-N + NO₃-N). Average soil extractable N was ≈ 60 kg N ha⁻¹ prior to 20 May, 1995. Following the N sidedress, average extractable N became much more variable due to method of application. Above ground whole plant samples were collected once a week starting on 9 May, 1995. Total dry mass, elemental N and C content, leaf area per plant, and leaf area index were determined for each week until harvest. This data confirms that soil NO flux measurements were made during a period (12 May to 15 June, 1995) of rapid vegetative growth and N uptake by the crop. The characterization data will be presented in different temporal formats (e.g. change in percent water-filled pore space) to facilitate comparison to temporal trends in measured soil NO flux and extrapolation to published models relating soil variables to predicted flux.

Biogenic Soil Emissions of Nitric Oxide and Nitrous Oxide Using a Closed Static Chamber During the NOVA-95 Experiment

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Nitric oxide (NO) and nitrous oxide (N₂O) are environmentally significant gases that play key roles in the chemistry of the troposphere (NO), stratosphere (N₂O), and global climate (N₂O). Biogenic soil emissions are an important global source for both of these gases. Measurements of biogenic soil emissions of nitric oxide and nitrous oxide using a closed static chamber were obtained during the NOVA-95 experiment (May - June, 1995). The simultaneous measurements of biogenic soil emissions of NO and N₂O provide important information on the utilization of nitrogen by soil microorganisms in an agricultural soil. These measurements were obtained from more than a dozen sites within the cornfield-some fertilized and some unfertilized control sites. Diurnal measurements were obtained at several of these sites to assess the impact of the diurnal soil temperature at the same site on the biogenic emission of these gases. Measurements were also obtained before and after rainfall on these sites. Nitric oxide emissions exhibited a range of more than two orders of magnitude during the experiment, from less than 1 to almost 200 nanograms of nitrogen meter⁻² sec⁻¹ (ng N m⁻² s⁻¹), depending on rainfall and fertilization. Highest soil emissions of nitrous oxide were obtained following a very strong rainfall, when the soil became saturated with water. The impact of soil temperature, soil moisture, and soil nitrogen on biogenic emissions of nitric oxide and nitrous oxide will be discussed. These measurements will be compared with measurements of biogenic soil emissions of NO and N₂O that we obtained on agricultural sites in Virginia and Colorado and from natural soils in very diverse ecosystems, including chaparral in southern California, savanna grasslands in southern Africa and boreal forests in Canada.

Measurements of Nitric Oxide Flux From Intensively Managed Agricultural Soil in the Coastal Plain of North Carolina

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Rural Photochemistry is influenced by Nitric Oxide (NO) emissions from agriculturally managed soils. The flux of (NO) was measured during a one month intensive measurement period in the coastal plain of North Carolina as part of Project NOVA during May-June 1995. NO emission rates were determined using a dynamic chamber system. Preliminary results indicate a range of fluxes from 4.18 to 253 ng N m⁻² s⁻¹ for NO. The fluxes were regressed against soil temperature, air temperature, water filled pore space, and extractable soil nitrogen; they showed a semi-logarithmic relationship with soil temperature. Fluxes of NOY and NO₂ were also calculated to ascertain the balance of nitrogen species being emitted. Ambient (10 meter) concentrations of NO, NOY, and O₃ were also measured along with wind speed and wind direction in an effort to gain insight regarding the local production and/or long range transport of these reactive nitrogen compounds.

Controlled Laboratory Studies of NO Flux Into the Lower Levels of the Troposphere Under Widely Varying Soil Conditions

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Controlled laboratory studies of NO emissions from soils are discussed which contribute to the understanding of the mechanical, chemical and biological mechanisms responsible for NO flux from the soil to the lower levels of the troposphere. Newly designed and constructed laboratory test chambers with attendant laboratory procedures are described. The results of tests conducted under widely varying soil conditions, including moisture, pH, temperature, and the presence of sunlight are presented. The information is referenced to data collected in field studies.

Eddy Correlation Measurements of NO, NO₂, and O₃ Fluxes

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The micrometeorological technique of eddy correlation was used to measure the vertical fluxes of NO, NO₂, and O₃ in rural North Carolina during the spring of 1995 as part of a collaborative effort on the natural emission of oxidant precursors validation of techniques and assessment (NOVA). The net mass flux densities were measured at heights of 5 m and 10 m above an agricultural field with short corn plants and large amounts of exposed bare soil between the rows. Large upward eddy fluxes of NO₂ were seen, and strong NO emissions from the soil were measured by collaborators using environmental enclosures on the soil surface. Preliminary calculations for midday observations indicated that about 50% of the nitrogen emitted from the soil was converted into NO₂ flux at a height of 5m, about 40% remained as NO flux, and 10% was returned to the vegetation and soil. Some divergence of the NO₂ and O₃ fluxes was detected between heights of 5 m and 10 m. These results are consistent with the likely net NO₂ production and O₃ destruction rates. Such data will be used to help develop parameterizations on NO_x flux into the lower troposphere.

Nitric Oxide Fluxes Observed Over A Fertilized Corn Field

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This group maintains a research site within the University of Maryland Wye Research Center, Wye River, Maryland located at 38 deg 54' N, 76 deg 14' W on Maryland's Eastern Shore. Continuous measurements at 10 m of meteorology, UV radiative flux, O₃, and CO have been made at this site for extended periods since 1993, sometimes enhanced with continuous measurements of NO and NO_x. From 13 July to 3 August 1995, NO emission fluxes using the technique of eddy correlation, along with additional complementary chemical data (mean CO, O₃, NO, NO_x) and UV radiative flux were measured at this site. Fast wind speed and temperature values were measured with a sonic anemometer. During this period measurements were made on a NOAA/ARL sampling tower at 6 m, above a fertilized corn canopy which was about 2.4 m tall by late July. From 25-30 July, 120 x 30-min. average sensible heat and NO flux values were computed. These results will be reported and interpreted in detail, with particular focus on characteristic behaviour at 24-hour and synoptic time scales. The mean (and median) NO fluxes for this time were 7.05 (and 7.34) ng N / m² / s, and values

ranged from -12.33 to 21.67 ng N / m² / s. Six of the 30-min. average flux values were negative; during these six periods, ambient observed NO mixing ratio was above 1 ppbv. This suggests that during these periods, the boundary layer was adjusting to a new equilibrium by depositing NO to the surface. The NO flux values compare favorably with similar measurements made over plots of fertilized soil.

Micrometeorology and Flux-Gradient Relation of NO-NO₂-O₃ System Near the Surface

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Eddy-correlation technique and dynamic chamber technique were employed at the same time and same location in an experiment in May 1995. In this paper, diffusivities of momentum, heat and water vapor as calculated from the micrometeorological data; are compared using the framework of the Monin-Obukhov similarity theory. The applicability of the theory to ozone and nitrogen dioxide is also investigated. The authors compare and discuss the fluxes between two different height levels and between two measurement methods with the objective of better understanding micrometeorological and chemical influences on the flux-gradient relationship of NO-NO₂-O₃ system in the atmospheric surface layer.

The Relationship Between the Surface Exchange Fluxes of Trace Species Determined by Enclosure and by Micrometeorological Techniques

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A major objective of the NOVA program is to characterize the measurement of fluxes by the dynamic enclosure technique. To this end the surface exchange fluxes of oxides of nitrogen and other species are determined using both enclosure and micrometeorological techniques. To complement the basic flux measurements, meteorological, micrometeorological, soil, chemical and radiation measurements are also made to characterize the total measurement environment. The fluxes measured by eddy correlation and the fluxes measured using enclosures are compared and an attempt is made to analyze the affect of introducing additional factors to effect a closure between the two different determinations. An examination of the other prevailing environmental parameters is made to enable us to define those conditions when the two methodologies can be brought into agreement. A simple numerical model relating the two measurement

methods under different conditions has been devised and is used to compare the observations by the two techniques brought into agreement.

Flux Measurements of Volatile Organic Compounds Over a Corn Field

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Vertical concentration gradients of volatile organic compounds (VOCs) were measured over a corn field, in its early growth period, during May 1995, in the coastal plains of North Carolina. These measurements were made as part of project NOVA (Natural emissions of Oxidant precursors: Validation of techniques and Assessment) to estimate the flux of VOCs. A modified Bowen Ratio technique was adopted for flux calculations. Average emissions of methanol, ethylene, α -pinene, β -pinene, and d-limonene were found to be 29.66 ± 20.06 , 20.68 ± 14.21 , 37.58 ± 37.28 , 9.37 ± 7.51 and 9.09 ± 5.28 $\mu\text{g}/\text{m}^2/\text{hr}$ respectively. Deposition velocities of certain anthropogenic hydrocarbons were also estimated.

Measurement of Soil Nitrous Oxide Flux from an Intensively Managed Agricultural Row Crop in the Lower Coastal Plain Region of North Carolina

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The ratio of soil nitric oxide (NO) flux to soil nitrous oxide (N₂O) flux is often used to determine the dominant process (nitrification or denitrification) associated with NO production in soils. This study, a part of the Natural emissions of Oxidant precursors: Validation of techniques and Assessment (NOVA) project - 1995, measured soil N₂O flux using PVC vented-cylindrical chambers (diameter-10.1 cm; height-10 cm) in an intensively managed agricultural row crop (corn - *Zea Mays*) from 19 May to 2 July, 1995. PVC sampling rings ($n = 64$; diameter-10 cm; height-10 cm) with beveled edges were installed to a depth of 8.5 cm in groups of 16 ($n=8$; row and interrow positions) at four locations within the sampling area two weeks prior to the start of the measurement period, and left in the same position for the duration of the study. Air samples were

obtained through a septum with a two-way needle into an evacuated glass septa bottle (125 mL) 25 minutes (10-15 minutes during periods of high N₂O using a gas chromatograph equipped with an electron capture detector. From 19 May to 4 June, 1995 (total rainfall < 1 cm), average soil N₂O flux was 15.8 (+/- 297) ng m⁻² s⁻¹ for the row and interrow positions, respectively, for the remainder of the study. Calculated N₂O fluxes > 2100 ng m⁻² s⁻¹ were observed immediately following (within 6 hours) rainfall events > 1 cm during this period. Based on the calculated N₂O flux relatively low, conditions which would favor NO production by nitrification. After 5 June, 1995, soil N₂O flux increased, suggesting that denitrification could have accounted for a substantial portion of the NO flux emitted during the remainder of the study period.

Biogenic Nitric Oxide Source Strengths

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Nitric Oxide (NO) emission rates were measured during the summer of 1995 at 4 different sites, representing major physiographic regions of the Southeast United States, in an effort to compare fluxes from agriculturally managed soils. Emission rates were determined using a dynamic chamber system. The measurement campaign began in the Coastal Plains region of North Carolina and progressed to the Upper Piedmont region of the state. Additional measurements included ambient (10 m) O₃, NO and NO_y concentrations, wind speed and direction. Soil temperature (at 5 cm depth) and air temperature were also recorded. Additionally, soil samples were taken which were analyzed for soil water content, bulk density, total extractable nitrogen and percent water filled pore space. Preliminary results indicate a range of fluxes from 1.21 to 78.57 ng N m⁻² s⁻¹ for NO. Intersite differences in NO flux reflect the differences in the amount of fertilizer applied to each of the soils. NO_y fluxes and NO₂ fluxes were also calculated in an attempt to ascertain the balance of nitrogen species being emitted.

Atmospheric Pollutant Deposition Over a South Central North Carolina Cornfield

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The National Oceanic and Atmospheric Administration Atmospheric Turbulence and Diffusion Division (ATDD) model was used to infer the dry deposition velocities of gaseous and particle pollutants, such as O₃, SO₂, NO₂, and sulfate and nitrate aerosols onto a cornfield in North Carolina (35.7° N, 76.8° W) during its growing season. The deposition velocity of ozone is in the range of 0 to 4 cm s⁻¹. The deposition velocities of both sulfur dioxide and nitrogen dioxide are in the range of 0 to 0.2 cm s⁻¹ with an average of 0.1 (±0.02) cm s⁻¹. Deposition fluxes are calculated and compared with other studies. The analysis of the data set is in progress.

Contributions of Meteorology on Ozone Behavior in Urban North Carolina

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As part of an effort by the state of North Carolina to develop a State Implementation Plan (SIP) for ozone control, a network of ozone stations was established to monitor ozone concentrations across the state. Approximately twenty-five ozone stations made continuous measurements surrounding the three major Metropolitan Statistical Areas (MSAs): Raleigh-Durham (RDU), Charlotte (CLT), and Greensboro - Winston-Salem - High Point (GSO). The relationship of meteorological parameters on the ozone behavior were analyzed during the summers of 1993, 1994, and 1995. A $\Delta(O_3)$ analysis (difference between the daily maximum [O₃] measured at an upwind and downwind site, which reflects the net increment of photochemical ozone added to an air mass as it advects over the city) was performed for high ozone days ([O₃] ³ 0.090 ppbv) in an effort to study if the current emission controls have been effective in urban regions of North Carolina. Synoptic and mesoscale analysis of key meteorological parameters were performed using data from the National Weather Service, AIR Sonde launches, and the Charlotte Wind Profiler, and it suggested that synoptic meteorology and urban photochemistry were important in analyzing high ozone days.

A Climatology of Regional Ozone: Meteorological Effects on Ozone Exceedences in the Southeast U.S.

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Implementing a plan for urban areas to meet the EPA's guidelines for ozone attainment continues to be a problem, particularly in the southeastern United States where vast spans of natural forest areas emit greater concentrations of biogenic hydrocarbons than in other areas of the country. While the EPA standards have been met for NOX and VOCs, ozone concentrations still exhibit large interannual variation, which is believed to be caused in part by differences in meteorological parameters. Ozone records were studied during the photochemically active season (April 01 - October 31 each year) for a fifteen year period from 1980-1994 at the five major Metropolitan Statistical Areas (MSAs) in the Southeastern United States (i.e., Atlanta, GA; Charlotte, NC; Nashville, TN; Raleigh, NC; and Greensboro, NC). From the hourly data, all ozone exceedences (concentration > 0.120 ppm) were recorded, along with a daily maximum concentration and a daily average concentration during the peak ozone production time of each day (10:00 am - 4:00 pm). Meteorological data studied in an effort to explain the interannual variation of ozone concentration include daily maximum temperature, and daily averages (from 10:00 am to 4:00 pm only) for wind speed, wind direction, temperature, pressure and relative humidity. Regional high pressure stagnation was also studied as an explanatory variable.

Regional Analysis of Non-Methane Hydrocarbons in the Southeastern United States

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Concentration of non-methane hydrocarbons as well as ozone, meteorological and trace gas data were measured at a network of eight rural sites located within the southeastern United States as a part of the Southern Oxidants Study. C2-C10 hydrocarbon were sampled once every six days from September 1992 through October 1994. The measurements were made in an effort to enhance the understanding of the behavior and trends of ozone and other photochemical

oxidants in this region. Biogenics display a maximum in the summer and minimum during the winter. Lower molecular weight alkanes and acetylene show a seasonal variation with a maximum during the winter.

Session 4

Aerosol Measurements

Chair: Petros Koutrakis, Harvard University, Harvard, MA

Attribution of College Park Aerosol Particulate Components by Size and Source

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Size-fractionated aerosol particulate samples in 6 discrete size intervals, ranging from <0.056 to $<15\ \mu\text{m}$, were collected with micro-orifice impactors (MOI) in the summer of 1990, in College Park, MD, a heavily-urban, nonindustrial area near Washington, D.C. Samples were collected on the roof the Meteorology building at the University of Maryland for 11 hours at a flow rate of 30 L \cdot min $^{-1}$ using Gelman "Teflo" filters as impaction substrates and backup filters. The first three stages ($D_{50}=1.8\ \mu\text{m}$) were coated with a thin film of dimethylpolysiloxane to reduce contamination of fine-particle stages with coarse particles. Selected samples were analyzed for 44 elements by instrumental neutron activation analysis using the NIST 20 MW research reactor with flux of $4.5 \times 10^{13}\ \text{n}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$. Chemical mass balance calculations were made on each of the stages of 17 MOI samples to resolve the ambient size distributions of aerosol mass and various elemental constituents of particles associated with 12 generic sources. Sulfur, V, and Zn were nearly exclusively attributed to distant coal-fired power plants (i.e., "regional sulfate"), oil combustion, and municipal incineration, respectively. Antimony and Cd were strongly associated with incineration, but had significant contributions from local coal combustion. Size spectra for regional sulfate, oil-combustion, and incinerator components were clearly different.

Resolution of Aerosol Constituents by Size and Source in the Urban Plume Over Lake Michigan

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Size segregated atmospheric aerosol samples were collected simultaneously

at three sites on and around Lake Michigan from July 17 through July 28, 1994: Chicago, IL, over Lake Michigan on board the EPA R/V Lake Guardian, and on the distant shore at South Haven, MI. Micro-orifice impactors (MOI) used for sample collection yielded 10 aerosol size fractions per sample ranging from <0.056 μm to 15 μm , and sampling followed a diurnal cycle of separate day and night collections. Gelman "Teflo" Teflon membrane filters were used as impaction substrates, and the first three stages of all impactor samples were coated with approximately 2 mg of Dow dimethylpolysiloxane grease to reduce coarse particle bounce. Twenty seven sets of MOI samples have been analyzed for >45 elements using X-ray fluorescence (XRF) and Instrumental Neutron Activation Analysis (INAA). Chemical mass balance calculations were made using data for each of the stages of a select group of these samples to resolve the size distributions of elemental constituents of particles associated with 12 generic sources.

Size Distribution of IR-Tagged Soot from Diesel Sanitation Trucks

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D. Poster

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A part of the U.S. EPA's great waters study of the influence of the Baltimore urban plume on water quality of the Chesapeake Bay, 100 g of iridium (III) acetylacetonate was used to tag 170 m³ of diesel fuel burned by the City of Baltimore's sanitation truck fleet during a 20-day period in August, 1995.

Aerosol emitted from the exhaust pipe of a single, rear-loading sanitation truck was diluted and size-fractionated into 10 discrete size intervals, ranging from <0.056 to <15 μm , and collected in a micro-orifice impactor (MOI). Each sample was collected continuously for up to 5 hours as the truck made its rounds. Samples were analyzed for elemental carbon by correlation with optical density, methylene chloride extractable organic material (EOM), and for the Ir tracer material by instrumental neutron activation analysis. Concentration vs size spectra contained broad peaks, presumably, resulting from changing combustion conditions during the operation of the truck.

Health Risks and Particle Monitoring: New Technologies to Meet Emerging Risk Management Needs

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EPA is reviewing the airborne particle standard, which is based upon associations with mortality and morbidity in communities. Particle levels during the 1952 London fog were 1,200 $\mu\text{g}/\text{M}^3$. Recent studies associate effects with levels within the standard, and below levels explained toxicologically. EPA must decide whether to control particles to levels below those of demonstrated toxicological significance. This study inquires whether 24-hour average levels might encompass undetected excursions which explain mortality.

Two monitoring technologies—inertial and beta attenuation—were found capable of measuring over short intervals. Both represent economical alternatives to gravimetric measurement. Data revealed 15-minute excursions reaching 2,000 $\mu\text{g}/\text{M}^3$.

Toxicology literature confirmed that particles in this range can harm. Persistent elevations must be more stressful than brief excursions observed here. However, particles within the 10-micron range are cleared inefficiently, especially by individuals suffering from respiratory disease. Consequently, short-term excursions of respirable particles may cause long-term internal dosing, and cardiopulmonary stress for susceptible individuals.

This study suggests that known toxicological mechanisms explain associations of particles with mortality if exposure is scrutinized over short intervals. However, the standard requires averaging over 24 hours, precluding detection and control of exposures which seem toxicologically significant. EPA may avoid strengthening 24-hour limits by imposing a less burdensome one-hour limit. This strategy appears to be health protective, justified by data, and feasible.

Harvard/EPA Ambient Fine Particle Concentrator for Conducting Human Exposures

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This paper presents the development and evaluation of an ambient particle concentrator for conducting human inhalation exposure studies. The system concentrates ambient particles in the size range 0.1-2.5 μm (aerodynamic diameter, d_p) by drawing them through a series of three virtual impactors. Each impactor contains the majority of ambient fine mass ($d_p < 2.5$ μm aerodynamic diameter) in a bleed flow (minor flow) that in the first two stages is 20% of the total flow entering the stage, while in the third stage is 50% of the total flow. A dilution system has been added to condition the temperature and relative humidity of the concentrated aerosol prior to supplying it to the exposure

chamber. The intake sampling flow is 5500 liters/min and the system delivers an aerosol enriched in concentration by a factor of 10 at 200 liters/min.

The virtual impactors were characterized using outdoor and indoor air samples as test aerosols. Fine mass and sulfate concentrations at the outlet of the concentrating system were compared to the ambient fine mass and sulfate levels, determined using Harvard-Marple impactors. The experimental tests have demonstrated that the overall concentration enrichment achieved by our system is by a factor of 8-11, depending on the average particle size of the sampled aerosol. Furthermore, the concentrated aerosol is delivered into the exposure chamber at a pressure of 0.94 atmospheres, thus making it possible to conduct human exposures at essentially atmospheric pressure.

Characteristics of Ambient Aerosols in Washington D.C. as Measured by Continuous and Time-Integrated Sampling Methods

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During the summer of 1994, an array of real-time continuous and integrated measurements of the concentration of particulate matter (PM_{10} and $PM_{2.5}$) were made at the Harvard/EPA monitoring station in downtown Washington, D.C. The Scanning Mobility Particle Sizer (SMPS) and the Aerodynamic Particle Sizer (APS) were used in conjunction to count continuously particles ranging from 0.02-30.0 μm . In addition, the study included real-time measurements of SO_4^{2-} and black carbon, as well as continuous PM_{10} and $PM_{2.5}$ measurements using the Tapered Element Oscillating Microbalance (TEOM). Furthermore, 3-hour integrated measurements of elemental and organic carbon were conducted using the Rupprecht and Pataschnick carbon monitor, and 24-hour integrated measurements of the particulate mass, sulfate, and nitrate size distributions were made using the Micro-orifice Uniform Deposit Impactor (MOUDI).

Diurnal concentration and particle size distribution patterns will be summarized for approximately 50 days of this study. The effect of relative humidity on real-time and integrated concentrations will be discussed. Furthermore, the effect of the relative humidity and particle concentration on the mass median diameter of the fine (0-2.5 μm) aerosol will be presented.

The Role of Transition Metals in Lung Injury After Air Pollution Particle Exposure

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We tested the hypothesis that a metal initially complexed to the surface of a particle could catalyze the generation of oxidants and be associated with an inflammatory injury of the lung. Polystyrene beads (0.945 μ m; Bangs Laboratories, Carmel, IN) with surface-COOH groups were treated with NaOH and then agitated in either 100 mM ferric ammonium sulfate (latex-Fe³⁺) or sterile water (latex) for 30 minutes. In vitro oxidant generation was measured as the absorbance of thiobarbituric-acid-products (A_{532}) in reaction mixtures including 1.0 mM H₂O₂, 1.0 mM ascorbate, 1.0 mM deoxyribose, and particles. Incubations with 1000 mg/ml latex-Fe³⁺ were increased relative to those including either an identical mass of latex or saline (A_{532} of 1.146 ± 0.036 , 0.372 ± 0.015 , and 0.093 ± 0.016 respectively; mean standard \pm deviation). Similarly, maximal luminol-enhanced chemiluminescence by rat alveolar macrophages (1.0×10^6 cells/ml) was elevated with exposures to 1000 mg/ml particles with complexed metal (3.0 ± 0.1 , 0.2 ± 0.1 , and 0.0 ± 0.0 V). Finally, 24 hours after intratracheal instillation into 60 day old, male Sprague Dawley rats, inflammation was significantly increased after latex-Fe³⁺ (lavage neutrophils of $37 \pm 11\%$, $16 \pm 9\%$, and $2 \pm 3\%$ and lavage proteins concentrations of 0.51 ± 0.05 , 0.26 ± 0.05 , and 0.11 ± 0.03 mg/ml). We conclude that metal initially complexed to the surface of a latex particle can be associated with increments in oxidant generation and lung injury.

Assessment of Air Toxic Emissions from a Pilot-Scale Combustion Unit

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The flue gas cleanup projects in the In-House Research program at the Pittsburgh Energy Technology Center (PETC) range from laboratory-scale work to testing with the combustion products of coal at a scale equivalent to about 0.75 MW of electric power generation. The largest unit is a 500-pound-per-hour (227 kg/hr), coal combustor, complete with ductwork, spray dryer, baghouse, and ancillary equipment. Over the past year, the unit has been upgraded and a number of shakedown tests have been conducted to prepare the unit for investigations of hazardous air pollutants, also known as air toxics.

These investigations of air toxics will be an integral component of the Air Toxics/Fine Particulate Control Subprogram administered by the Office of Project Management at PETC. The overall goal of this subprogram is to develop

innovative control techniques capable of reducing emissions of air toxics and fine particulate from sources utilizing fossil fuels to levels which result in negligible or acceptable risks to human health and the environment. A major effort within this subprogram to date has been the comprehensive assessment of toxic emissions from selected coal-fired electric utility units. Based on the results and conclusions from this effort, the study described in this paper focussed on trace elements and halogens.

The operation of a 500-pound-per-hour (PPH), pilot-scale combustion unit has now been characterized in terms of the formation, distribution, and fate of air toxics. The coal fired during the air toxics testing was from the same coal batch that had been fired in a full-scale utility boiler during an earlier assessment of air toxic emissions. A description of the pilot unit and operating conditions during the air toxics testing is provided, along with a summary of the test results. A comparison of the concentration of trace elements associated with the vapor phase, solid/particulate phase, and particulate size fraction is made with the results from the full-scale utility. Calculation of material balances around the pilot combustion unit, the baghouse, and the overall system as well as baghouse removal efficiencies are also provided. Based on the results of this air toxics characterization effort, the 500 PPH unit has been shown to be a valuable facility for comparison of sampling methods, development of continuous emissions monitors, and evaluation of air toxics control systems.

Diurnal Variations in Particulate Mass and Total Sulfate Concentrations at a Site in Metropolitan Philadelphia

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Most measurements of particulate mass and sulfate concentrations have been based on samples collected over periods of 24 hours. An accurate exposure assessment, however, requires diurnal distributions of ambient particulate matter. As part of the Metropolitan Aerosol Acidity Characterization Study, hourly concentrations of PM₁₀, PM_{2.5}, and total sulfate have been measured at a site in Metropolitan Philadelphia area during the summer of 1992. PM₁₀ and PM_{2.5} have been monitored using the Rupprecht and Patashnick model 1400 Tapered Element Oscillation Microbalance (TEOM®). Semi-continuous (10 minute time resolution) measurements of total sulfate have been done by using a method named the Harvard Continuous Sulfate/Thermal Speciation (CSTS) system.

Examining diurnal variations in concentrations of total sulfate, PM₁₀,

PM_{2.5}, and coarse fractions of PM₁₀ (i.e., PM₁₀-PM_{2.5}), we have observed that total sulfate and PM_{2.5} had a similar diurnal pattern: the peak concentrations typically occurred in the afternoon unless the previous day had had much higher peak concentrations which might remain for a few hours up to the next morning. We have also calculated monthly means (and c.v.) of particulate mass and sulfate concentrations for each hour of the day. Based on these monthly means, we have conducted statistical analyses to study relationships among different fractions of particulate matter measured, leading to a better understanding of diurnal distribution of particulate matter in urban Philadelphia area.

A Field Assessment of the Effect of Volatile Constituents on the Measurement of Ambient Particulate Matter Mass Concentration

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Recently, airborne particulate matter has been receiving increased attention as published epidemiological health studies have heightened the concern over associated human health-related issues. The current court-ordered review of the particulate matter standard in the United States is just one example that has increased focus on the collection, measurement and identification of ambient particulate matter.

With particulate matter, unlike criteria gaseous pollutants, a potential exists for what is defined as particulate matter to change its mass as a result of unstable residence on the filter due to light volatile substances (e.g. water, secondary aerosols, aromatic hydrocarbons, organic carbon) associated with the particulate matter and filter media. Some have speculated that particulate matter retention will become an acute issue with the U. S. EPA planning to add a fine particulate matter (PM_{2.5}) 24-hour and annual standard to the current PM₁₀ annual standard in 1997.

This paper discusses some of the critical aspects of particulate matter measurements. In addition, field data are presented to identify the role that key parameters such as sampling and equilibration temperature, relative humidity, and filter face velocity may play in the quantification of particulate matter mass concentration. Supporting measurements of several particulate matter chemical constituents during episodic events are used to quantify their contribution.

Pulmonary Toxicity of Urban Air Particulate Matter (PM)

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Alan Hoffman

NERL, U.S. EPA

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A. Osornio-Vargas

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Identification of toxic constituent(s) of urban air PM would provide some insight into the adverse health effects associated with exposure to this component of air pollution. We found that similar extent of acute pulmonary inflammation could be produced in rats exposed to different amounts of various urban air PM samples containing the same amount of transition metal. Additional *in vitro* cellular toxicity studies performed on PM₁₀ samples obtained from Mexico City identified the most cytotoxic PM₁₀ sample to contain the highest amount of transition metal, sulfate and soluble transition metal. Subsequent *in vivo* toxicity studies conducted on size-fractionated ambient air PM found the <1.7 μ m fraction to induce a greater degree of acute lung injury when compared to the 1.7-3.7 and 3.7-20 μ m size fractions. The <1.7 μ m fraction was the most acidic and contained the highest content of sulfate and soluble transition metal. These results indicate that particle size, metal content and bioavailability contribute to the pulmonary toxicity of urban ambient air PM.

Development of the New Federal Reference Method for Fine Particles: Current Methodology

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The U.S. Environmental Protection Agency (EPA) is reviewing the criteria and the National Ambient Air Quality Standard (NAAQS) for Particulate Matter (PM) under a court ordered schedule.

A key element in consideration of a revised standard will be sampling for fine particles in addition to current PM₁₀ requirements. This would result in the need for a new federal reference method (FRM) for fine particles. The approach the EPA has formulated requires the use of a single reference method (by design only) and provides for equivalent sampling based on the results of performance testing of other samplers in comparison to the designated reference method. The reference method will be freely available and published in the Federal Register. Equivalency specifications include wind tunnel testing, static laboratory tests, and field comparisons.

The currently planned components of the FRM for fine particles include: a wind speed independent sampling head; two serial impactors, at 10 and 2.5 mm; a 24 hour measuring period; allowance for automated sequential operation;

integrated realtime volumetric flow control; particle mass collected on a filter allowing for later chemical analysis; ability to operate under wide range of ambient conditions (temperature, humidity, and pressure); a sharp cut at 2.5 μ m; and mandated quality assurance requirements to insure high field network precision.

Session 5

Canisters

Chair: Eric Winegar, Air Toxics Limited, Folsom, CA

Passive Flow Controllers: Revisited - Per EPA Method TO-15

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Abstract not available.

Fourteen-Day Stability of 27 Polar VOCs In Summa® and Silocan™ Canisters

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Both SUMMA® and SilcoCan™ passivated stainless-steel canisters can be used effectively to determine ppb and sub-ppb concentrations of non-polar volatile organic compounds (NPVOCs) in ambient air using the sampling and analysis procedures described in Compendium Method TO-14. SUMMA® passivation of the interior metal surface of a canister involves electropolishing techniques while SilcoCan™ passivation involves coating with a sub-micron layer of inert fused silica. A comparison study was performed to determine the stability of 27 polar VOCs (PVOCs) over a 14-day period in both SUMMA® and SilcoCan™ canisters. PVOCs are generally more reactive than NPVOCs and have a greater potential for adsorption with active sites on the interior surface of canisters.

A gaseous standard containing a mixture of the 27 PVOCs at approximately 100 ppbV each in nitrogen was prepared by Scott Specialty Gases in a high-pressure cylinder. Pressurized canister samples (3 SUMMA® and 3 SilcoCan™) were prepared at 5 ppbV by dynamic dilution of the Scott mixture with humidified ultra-pure grade air. Canisters were analyzed by GC/MS-SCAN. Sample moisture management without coremoval of PVOCs was performed using an Entech preconcentrator configured with a multi-stage trapping technique. Samples were analyzed on Days 0, 3, 10, and 14. The temporal stability of individual PVOCs is graphically presented by plotting their average relative response factors against the day analyzed.

Development of an Intelligent Canister/Cartridge Sampler for the Collection of Ozone or Air Toxics

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In 1993, we designed and built an intelligent sampler capable of collecting eight canisters and eight DNPH-cartridges daily, to meet rigorous Enhanced Ozone Monitoring requirements for Southeastern Wisconsin. Working from the multicartridge/multicartridge sampler design, we have developed a smaller sampling unit to collect samples for ozone precursors, reformulated fuel additives, and general air toxics. A site-based computer will track all samples from the sampler setup, through sampling, to sampler take down. Relevant sampling data such as initial canister vacuum, final canister pressure, and sampling flow rates are all recorded by the sampler. At the completion of the sampling episode all sampling data are down loaded to the project database. Software for the original sampler and new sampler has been revised to include internal and external Quality Assurance procedures. We will report on the design of the new sampler, important software revisions, and the sampler performance during an initial season of sampling.

The Use of Fused Silica Lined Canisters for Difficult Ambient Air Samples

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Many compounds in ambient air have been difficult to collect and analyze from SUMMA canisters. These difficult compounds include both polar and sulfur compounds. Many polar compounds, such as alcohols, ketones, and aldehydes are being considered for EPA Compendium Method TO-15. Sulfur compounds such as hydrogen sulfide, methyl mercaptan, dimethyl disulfide, and COS have been a constant struggle for analysts with SUMMA canisters.

This paper describes work in which we used fused silica lined canisters, SilcoCans, for the collection and analysis of polar and sulfur compounds. We will also discuss the importance of an inert sample pathway for these compounds. We will be discussing the use of a fused silica lined valve to ensure an inert sample pathway. Data will be used to demonstrate the stability and holding times of many of these polar and sulfur compounds within SilcoCans and silcostepped valves.

PPBV Determination of Reduced Sulfur Compounds using Glass Lined Canisters, Deactivated Tedlar Bags and Sorbent Tubes: A Study of the Critical Parameters

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Many reduced sulfur compounds are quite reactive which often makes them difficult to properly sample, transport and analyze. Current methodologies utilize Tedlar bags as a sampling media and analysis based on gas chromatography (GC) and selective detection; that is, flame photometric (FPD) or sulfur chemiluminescence (SCI) detectors. Existing methods caution the analyst to frequently check the calibration and take every step to ensure system inertness. While the overall performance of the analytical system is important, the lack of precision in the measurement can be attributed to the instability of many sulfur compounds in Tedlar bags.

This work investigates various means of collecting and transporting the sample prior to analysis. Several new technologies are available for collecting an air sample containing reactive compounds. Among these are glass lined stainless steel canisters, various new carbon based sorbents and deactivated Tedlar bags.

This work on sample stability utilizes GC/SCD because of the selectivity, sensitivity, equimolar response and linearity of the SCD. Several sampling containers were investigated including untreated glass lined canisters, deactivated glass lined containers, deactivated Tedlar bags and newly developed carbon based sorbents. Response factors are used to determine holding times for various sulfur compounds. The relative influence of environmental factors such as concentration, relative humidity and hydrocarbon background are included in the investigation.

A Through-The-Probe Toxic Audit Study to Determine the Effect of Moisture on Volatile Organic Compound Recovery Rates in Stainless Steel Canisters

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Through-the-probe audits of volatile organic compounds (VOC) have been a part of the ambient toxic program in California since 1988. By introducing known quantities of VOCs at the probe inlet, the audits check the integrity of the field probe, the toxic sampler (leaks, contamination, etc.), the transport system (sample canister), and the laboratory analysis accuracy of the canister contents. Until 1993, auditing was performed using dry audit gases in dry, clean stainless steel canisters. Recovery rates for several aromatics, in particular, were low

when compared to audit samples introduced directly into laboratory instruments. To improve VOC recovery rates, a field study was conducted which compared dry canister auditing with canisters injected with HPLC water (50 to 100 ul). This change improved the recovery of most compounds, yet not adequate for the needs of an audit program.

This paper contains a report on work to date to extend the audit development program to increase VOC recovery rates in SUMMA canisters by using in-line humidification. An in-line bubbler was installed in the through-the-probe toxic audit train to humidify the dry air which dilutes the toxic audit gases. This approach more closely mimics ambient sampling conditions by humidifying the entire audit train and sampler probe line, potentially improving VOC recovery rates over the water-injected canister method. The goal of both studies was to improve our ability to assess the data accuracy for the ambient toxics and PAMS programs. Currently, the in-line humidification study employing dry sample canisters is still in progress and yield results are incomplete. This paper presents the results of the wet-injected canister study.

Meeting the Technical Acceptance Criteria for TO15 Methodology Using a New Canister Autosampler

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Approximately 108 of the Hazardous Air Pollutants (HAPs) specified in the 1990 Clean Air Act Amendments (CAAA) are classified as volatile organic compounds (VOCs). Of the 108 volatiles, nearly 35% are oxygenated or polar compounds. While more than one sample introduction technique exists for the analysis of these air toxics, only canister sampling provides a medium for the complete range of analyses. A broad concentration range of polar and non-polar, and low and high molecular weight species can be analyzed from canisters. Additionally, duplicate samples can be taken from a single canister, samples can be diluted, and storage stability in canisters for many of the compounds listed has been demonstrated.

Until the introduction of Compendium Method TO15, few quality assurance/quality control criteria were specified within air methods. This paper demonstrates the technical acceptance objectives outlined in the TO15 methodology including mass spectral ion abundance criteria, initial calibration, daily calibration, blank analysis, laboratory control samples, and method detection limits. A novel technique for managing high levels of moisture and carbon dioxide commonly present in source samples is proven. Components analyzed include a representative mixture of polar and non-polar species from the TO14, CLP Statement of Work, and TO15 analyte lists. The analytical system consists of a Tekmar AutoCan Canister Autosampler interfaced to a Hewlett Packard 6890/5972 MSD.

Improved Methodology for Analysis of Ambient Level Reactive Sulfur Compounds

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Compounds with the formulas R1-S-R2 and R1-S-S-R2 have been very difficult to sample, store, and analyze due to their highly reactive properties. Having the same number of valence electrons as oxygen, sulfur tends to also be polar thus favoring interactions with active sites on surfaces. The valence electrons in sulfur atoms, however, are not held as close to the nucleus and are therefore much more influenced by localized charges. This decreases the activation energy necessary for adsorption to surfaces. Shielding the sulfur atom with bulky alkyl groups can reduce the reactivity of sulfur compounds through an electron donating effect, and maybe even more importantly by the added steric hindrance offered by the adjacent C-H(x) groups that reduce the acceptable trajectory (cone of acceptance) for a potential reactant or reaction site. The reduction in the steric hindrance by replacing the alkyl groups with hydrogens probably accounts for the relative increase in reactivity in the following series:

Dialkylsulfides < Mercaptans < Hydrogen Sulfide.

Sampling, storing, and preconcentrating these compounds requires the near elimination of surfaces with ionic or highly polar characteristics (ie - active sites). Low temperatures must also be maintained to reduce the population of sulfur compounds with energy levels high enough for reactions to occur. For this reason, cold trap dehydration has been reported previously as a preferred method for eliminating water with minimal sulfur compound loss.

A modified, whole air approach for sampling and preconcentration will be presented that improves the recovery and analysis of ppb level mercaptans and hydrogen sulfide by GC/MS. Three different flow systems will be compared for their ability to reproducibly transfer sulfur compounds to the GC during preconcentration, including one comprised to nearly 100% teflon. Recoveries will be presented using sorbent and cryogenic based preconcentration and water management systems. A modified Cold Trap Dehydration procedure will be introduced that reduces sulfur compound that are normally occluded within forming ice crystals in the cold trap. Stability in specialty treated Canisters will also be investigated.

Innovative Flow Controller for Time Integrated Passive Sampling using SUMMA Canisters: Design, Testing and Applications

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To restrict the entry of gas inside evacuated vessels such as SUMMA canisters, mechanical flow controllers are used to collect integrated atmospheric samples. From the passive force given by the pressure gradient, the motion of gas can be controlled to obtain a constant flow rate. Presently, devices based on the principles of critical orifices are used and they are all limited to an upper integrated sampling time. We have recently developed a novel flow controller which can be designed to achieve any desired sampling time when used on evacuated vessels. It can extend the sampling time for hours, days, weeks or even months for the benefits of environmental, engineering and toxicological professionals. The design of our controller is made from computer simulations done with an original set of equations derived from fluid mechanic and gas kinetic laws. Sampling and analytical testing was performed, static and dynamic validation studies were also made in the laboratory. Since now, the experimental results showed excellent agreement with predictions from the mathematical model, and validation studies have proved its validity. This new controller has already found numerous applications. Units able to deliver a constant sampling rate between vacuum and approximately -10 inches Hg during a continuous seven days period have been used with SUMMA canisters of different volumes (100 ml, 500 ml, 1 liter and 6 l). From our research work, any combinations of sampling times for any sampler volumes are made possible. The innovative flow controller contributed in air quality assessment of ambient air around a sanitary landfill (indoor/outdoor), and inside domestic wastewater and pulpmill sludge treatment facilities. It is now proposed as an alternative methodology for atmospheric sampling in the russian orbital station Mir. The development of this device applied in sampling methods can now offer true long term passive monitoring of selected gaseous air pollutants.

Poster Session

Low-Level Analysis of Cr⁺⁶ in Air by Ion Chromatography

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A major difficulty in the analysis of air samples is in obtaining the sensitivity necessary to measure the analyte of interest. Many results obtained for the analysis of air samples are less than the limit of quantitation. This is particularly true for the analysis of hexavalent chromium (Cr⁺⁶) in air.

A Dionex DX 500 ion chromatograph was configured to determine Cr⁺⁶ in air. The flow rate of the mobile phase (0.2 M (NH₄)₂SO₄/0.1 M NH₄OH) was 1.4 mL/minute and a post column addition of diphenylcarbohydrazide (0.5 mL/minute) was made to complex the Cr⁺⁶ for detection at 520 nm.

A guard column (Dionex NG1) was installed prior to the separator column (Dionex AS7). To increase sensitivity, a concentrator column (Dionex AG7), which was loaded with 10 mL of sample prior to injection, was used instead of a sample loop.

When using the concentrator column, the limit of quantitation for Cr⁺⁶ in air was reduced to 10 ng/L. This is nearly a 100 fold increase in sensitivity as compared to using a 100 L sample loop. A linear calibration range to 500 ng/L was demonstrated.

The Significance of Hydrocarbons in the C₁₀-C₂₀ Range to Mass Contribution and Ozone Forming Potential During the COAST Study

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In order to improve the technical basis for designing effective ozone strategies for the Houston-Galveston and Beaumont-Port Arthur-Orange areas of southeast Texas, the Texas Natural Resources Conservation Commission (TNRCC) sponsored the Coastal Oxidant Assessment for Southeast Texas (COAST) project. Part of this study was to assess the significance of hydrocarbons in the C₁₀-C₂₀ range and determine their potential for ozone formation. Field measurements of volatile organic compounds (VOC) included the collocated sampling of canisters (C₂-C₁₂ range), and Tenax-TA (C₈-C₂₀ range) for ambient and source measurements. To assess the significance of hydrocarbons in the C₁₀-C₂₀ range, data from collocated canister and Tenax-TA measurements were merged and composite profiles developed. The profiles consist of data from C₃-C₂₀, with C₃ to n-octane obtained from canisters and n-octane to C₂₀ obtained from Tenax-TA. The relative ozone forming potential was developed by

multiplying individual hydrocarbon weight amounts by the appropriate maximum incremental reactivity (MIR) factor. These values were then normalized by dividing through by the base reactivity (sum of all reactivities) to yield percent contribution values.

The Application of High Speed Gas Chromatography to Air Analysis

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The requirement for continuous emissions monitoring for ambient or indoor air pollutants at industrial sites and ambient air at hazardous waste sites demands very short analysis times. While Gas Chromatography is a major monitoring technique, standard GC methods generally have long cycle times from 15 to 60 minutes. The demand for frequent sampling (2 to 5 minutes) approaching a continuous mode has generated interest in high speed GC analysis. But constraints imposed by the use of narrow bore (to 100 μ m i.d.) columns, namely sample capacity and instrument incompatibility, have impeded acceptance of this technique for this application.

This poster describes an apparatus which produces a minimum injection bandwidth (10 to 50 msec) which provides the primary means of attaining good column efficiency while achieving High Speed GC Analysis. This FastGC inlet which is mounted on a Varian 3400 Gas Chromatograph is described and its operation is detailed from the cyrofocussing of the sample onto a short Nickel tube to the 100,000° C/sec desorption to the 8 Meter x 0.32 mm capillary column. With the very narrow injection bandwidth, high hydrogen carrier velocities, and the short capillary column, the FastGC inlet is shown to provide analysis times of less than one minute for a number of applications of interest. In addition the high compound signal to noise ratios obtained requires sampling times of only one to two minutes to obtain sensitivities approaching one ppbv.

Applications described in the poster include chlorinated hydrocarbons, polar organics, an ozone precursor standard (C2 to C13), and BTEX's. Data regarding the recovery, response linearity, and retention time and area count precision are also reported.

Photochemical Assessment Monitoring: Overview and Data Analysis Activities

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In accordance with the Clean Air Act Amendments of 1990, EPA developed rules for the initiation of Photochemical Assessment Monitoring Stations (PAMS) by State and local air pollution control agencies located in serious, severe, and extreme ozone nonattainment areas. These PAMS networks monitor for a target list of volatile organic compounds (VOC) including several carbon-yls, as well as ozone, oxides of nitrogen, and surface/upper air meteorological measurements..

This poster will provide an overview of the monitoring requirements for the PAMS program and provide a few illustrations of data analysis techniques for the substantial and complex data base generated by the array of PAMS located in 22 affected areas across the United States.

A Novel Method of Measuring Ambient Aerosol Aspiration Efficiencies Using Phase Doppler Anemometer

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ManTech Environmental Technology, Inc.

In this study, a novel method has been developed to measure the aspiration efficiency of a sampling inlet using mass balance principles. Phase Doppler Anemometry (PDA) measurements are performed in proximity to a thin-walled sampling inlet. These measurements are non-invasive, requiring no physical sampling instrument, thus producing no perturbations in the aerosol flow. The measurement area is described by spherical surface enclosing the inlet. The velocity vector for each particle entering and leaving the sphere is measured. For a given sampling condition the overall mass flux is zero. The aspirated aerosol represents the fraction of the aerosol withdrawn from the environment. The integrated aerosol characteristics such as particulate mass, number concentration, and size distribution remain unchanged during the sampling process.

The aspiration efficiency of a sampling inlet is the first potential factor that can cause changes in aerosol characteristics during a sampling process and can contribute to a non-representative sample. Changes in the aerosol are caused by the difference in inertial properties between aerosol particles and gas molecules. Particles may not follow the fluid stream lines, thus do not enter a sampling inlet representatively causing an aspiration error.

Traditionally, trajectory or comparison methods are used to measure the aspiration efficiency of a sampling inlet. The trajectory method uses visualization of fluid streamlines and direct observation of particle deviation to assess aspiration. It requires laminar flow conditions and has only been applied to studying simple sampler systems. The comparison method requires two sets of

measurements, first, isokinetic samples where the fluid is disturbed as little as possible and second, the sampling method of interest. The isokinetic samples are assumed to have no aspiration error. The comparison method may be applied over a wider range of experiments. Its major disadvantages include the confusion of aspiration and apparent efficiencies and the difficulty of generating large amounts of uniformly distributed mono-dispersed particles in a large wind tunnel.

An argon-ion Phase Doppler Anemometer was utilized to measure the flux of polydispersed particles generated by a fluidized bed system. The flux is then converted into the aspiration efficiency by comparing the movement of small particles, representing fluid streamline motion and the large particles possessing sufficient inertia to generate an aspiration error. Isokinetic, sub-isokinetic, and super-isokinetic sampling processes have been studied. The results are in good agreement with those of Belyaev and Levin (1974).¹ The major advantage of this new method is that particles are generated locally and they do not need to be mono-disperse and uniformly distributed across the test area of the wind tunnel. Phase Doppler Anemometry can distinguish the size and the velocity of each individual particle. The sampling duration of the experiments are, therefore, significantly reduced and significant additional information is collected on the velocity vector distribution of the particles.

1. Belyaev S. P. And Levin L. M. (1974), "Techniques for collection of representative aerosol samplers." *J. Aerosol Sci.* 5, 325-338.

Methods Development for Clean Air Act Amendment Hazardous Air Pollutants from Stationary Sources: Methanol and Isocyanates

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Passage of the Clean Air Act Amendments of 1990 by the U.S. Congress delegated responsibility to the U.S. Environmental Protection Agency for the development of methodology required to monitor and protect the environment from 189 hazardous air pollutants (HAPs) listed for regulation. Contained in the list of the 189 HAPs are methanol and four isocyanates (2,4-toluene diisocyanate [TDI]; hexamethylene 1,6-diisocyanate [HDI]; methylene diphenyl diisocyanate [MDI]; and methyl isocyanate [MI]). The Methods Branch of the National Exposure Research Laboratory in Research Triangle Park, North Carolina has recently developed the methodology required to monitor these HAPs in stationary source emissions. A summary of the methodology developed and projects currently in progress will be reported at the Methods Branch poster session

during the EPA/AWMA Symposium for the "Measurements of Toxic and Related Air Pollutants," May 7-10, 1996.

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Methods Development for Clean Air Act Amendment Hazardous Air Pollutants from Stationary Sources: Methanol and Isocyanates

VOST Charcoal Specification Study

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The volatile organic sampling train (VOST) methodology incorporates SW-846 sampling Method 0030 and SW-846 analytical Method 5040 or 5041. VOST is currently one the leading methodology's available for the sampling and analysis of volatile principal organic hazardous constituents (POHCs) and products of incomplete combustion (PICs) from stationary sources at very low levels. However, revisions to the original method are necessary to maintain VOST as a viable regulatory tool. Method 0030 states that the VOST sampling tube set must consist of a front tube containing Tenax® (a 2,6-diphenylene oxide polymer) and a rear tube containing sequential bed of Tenax® and SKC Lot 104 petroleum-based charcoal "or equivalent." However, the method does not identify a specific equivalent, nor does the method supply the performance specifications which would allow determination of an equivalent. Lot 104 petroleum-based charcoal is no longer commercially available and has not been available for several years. Laboratories are presently using a wide range of substitutes, usually coconut-based charcoal, and there is a wide range of performance from batch to batch of charcoal in one laboratory and from laboratory to laboratory. To provide performance specifications and identify a replacement for SKC Lot 104 charcoal, a VOST charcoal specification study was initiated. The following carbon-based candidate sorbents were considered: Tenax-GR (a graphitized Tenax); a Petroleum-based Charcoal; Ambersorb® XE-340 (hydrophobic carbonized resin bead); Anasorb® 747 (beaded active carbon with very regular pore size); Carbosieve® S-III (carbon molecular sieve); and a Beaded Activated Charcoal (BAC)(with a very regular pore size).

The results indicated that Tenax-GR showed significantly poorer performance than the other candidates in preliminary experimental results. Ambersorb did not retain the gaseous volatile organic compounds tested as well

as the others and recovery of vinyl chloride was very low at all levels of spiking. Carbosieve was eliminated as a candidate replacement because of cost and handling problems. The petroleum-based charcoal was eliminated because of difficulties in handling a finely-divided powder. The availability of Anasorb 747 proved to be the deciding factor between it and the BAC. Performance, cost, ease of handling, and plentiful supply make Anasorb® 747 a good choice for replacement of SKC Lot 104.

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Method Evaluation Study: The Application of SemiVOST to the Nonhalogenated Semivolatile Organic Compounds from the Clean Air Act Amendments

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A laboratory study and three field studies were performed to evaluate the application of the SemiVOST (EPA sampling Method 0010, EPA sample preparation Draft Method 3542, and EPA analytical Method 8270) to the semivolatile halogenated organic compounds (approximately 80 compounds) listed in the Clean Air Act Amendments (CAAA) of 1990. In these initial studies, PCBs, dioxins, and pesticides were excluded. Subsequently, a laboratory study was performed to assess the feasibility of the application of the SemiVOST methodology to the semivolatile nonhalogenated organic compounds listed in the CAAA (approximately 70 compounds). Several of the semivolatile organic compounds were eliminated from consideration as SemiVOST analytes because they could not be analyzed successfully by gas chromatography/mass spectrometry (GC/MS), reacted with other compounds in solution, or were insoluble in methylene chloride at the levels required to perform dynamic spiking in the field. The remaining CAAA semivolatile organic analytes were grouped as acid/neutrals and base/neutrals and evaluated in the field using the guidance of EPA Method 301 for experimental design and statistical evaluation of the data. Quadruple SemiVOST trains were run in the field, with dynamic spiking of the semivolatile analytes from a methylene chloride solution of either acid/neutrals or base/neutrals into two of the sampling trains. The bias and precision of the overall SemiVOST methodology (sampling, sample preparation,

and analysis) applied to each of the semivolatile organic analytes were evaluated.

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Development of a Source Test Method for Measurement of Mercury Species

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The lack of a validated speciation method for stack emitted mercury, according to the Draft Report to Congress, is a critical information gap in methodologies to assess human and ecological exposures (and consequently risks) associated with such mercury. Because no validated method exists, current assessments must rely on unvalidated assumptions as to the species distributions to estimate environmental concentrations and ultimately exposures. The present study deals with research on the development of a method to speciate mercury emissions.

EPA Method 29 and modified versions were studied to assess their mercury speciation capability. It was speculated that the bulk of ionic mercury species should be collected in the upstream acidified peroxide impingers due to the high solubility in water of HgCl_2 , while the relatively insoluble elemental mercury should pass through to the acidified permanganate collectors. The studies were carried out using simulated flue gas which included sulfur dioxide (1000-2000 ppm), hydrochloric acid (100 ppm), water vapor (10%), carbon dioxide (10%) and nitric oxide. Ionic and elemental mercury vapors were obtained using permeation tubes.

Initial tests with Method 29 indicated that small amounts (3%) of Hg^0 were collected by the hydrogen peroxide/nitric acid impingers. This percentage increased with increasing sulfur dioxide concentrations. However, when water was substituted for the acidified peroxide reagent in the first two impingers, the speciation was very clean, with greater than 99.9% of Hg^0 passing through the water impingers to be collected in the permanganate even when sulfur dioxide was present. Details of this study are given.

FT-IR Transmission Spectroscopy for Quantitation of Ammonium Bisulfate in Fine-Particulate Matter Collected on Teflon® Filters

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A quantitative measurement method for the determination of fine-particle bisulfate in ammonium bisulfate collected from the ambient air onto Teflon® filters is described. Infrared absorbance measurements of the Teflon® filters are made before and after particle collection. Subtraction of the two spectra reveals the absorbance spectrum of the particles. The presence of bisulfate is identified by characteristic and unique spectral features including prominent absorption bands at 1050 and 870 cm^{-1} is used for quantitation. The lower limit of detection for the bisulfate ion is 150 nanomoles. This amount corresponds to the ammonium bisulfate which would be collected from an air volume containing 1.2-microgram/ m^3 samples for 24 hours at 10.0 L/min. This method provides a specific, nondestructive, direct measurement of ammonium bisulfate.

Organic Compound Delivery Device

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The design and implementation of a transferring device for delivery of organic gas phase sample to GC or GC/MASS SPEC instrumentation. The device is simple in design, economical to build, with low maintenance requirements. The device is easily installed with minimal downtime to instrumentation. Testing of design is conducted using a specific range of selected organic compounds. Components of design were assembled from "off-the-shelf" purchases of materials. The main objectives include valve options, primary trap design, carrier-gas flow rates, temperature parameters, and method development as appropriate. The end product is specifications and Assembly instructions coupled with standard operating procedures (SOPs) available upon written request from EPA, NERL, R.T.P.

The use of this device could greatly increase the consistency and validity of analytical data between laboratories, especially multi-lab studies.

The target audience would be "all" laboratories using GC/MS instrumentation for sample analysis.

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Marine Crustaceans as Indicators of Estuarine Health - *The Atlantic Blue Crab (Callinectes sapidus)*

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In 1993 AREAL, later NERL, in conjunction with N.C. State University, School of Veterinary Medicine, N.C. State Government DEHNR/Div. of Marine Resources, Dr. Marius Brower Duke University School of the Environment and Region III, began a multimedia study centering around the Blue Crab and other estuarine media to develop multimedia analytical methodology and to determine if selected marine crustaceans could serve as bioindicators of estuarine deterioration. The Blue Crab was selected because of the association of a bacterial mediated disease (soft shell disease) and water pollution. The questions posed in the study were; is water pollution affecting the immune systems of marine crustacea; are chemical pollutants in the water affecting the development of the chitinous exoskeleton of crustaceans making them more susceptible to attack by chitinoclastic bacteria; what role do trace elements play in this process, and, would selected marine crustaceans serve as bioindicators of a deteriorating estuarine environment.

Multimedia Analysis by Pyrolysis/Gas Chromatography/Mass Spectrometry

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The analysis of organic species in environmental samples is usually complex and time consuming. The types of techniques and methods used are selected depending on the matrix and the target compounds being analyzed. The development of fast, precise, reliable, flexible and ideally multimedia analytical procedures is desirable. Pyrolysis coupled to a gas chromatograph/ mass spectrometer (Py/GC/MS) has these characteristics.

Pyrolysis can be applied to synthetic polymer chemistry, natural products, microbiology, etc. Today platinum (Pt) filament instruments can be easily coupled to a GC and used to perform classical pyrolysis and/or thermal desorption of the compounds from a given matrix. The technique can be applied to the analysis of soil, sediment, tissue, sewage, and other matrices offering a unified approach to environmental analysis. Some matrices studied in the laboratory include tissue, sediment and particulate matter.

This work evaluates Py/GC/MS as a fast economical screening technique for polycyclic aromatic hydrocarbons (PAHs) in sediment samples. The effects of different temperatures, gas flows and times, solution port injections and interface

injections, packed quartz tubes, open boats and ribbon volatilization were considered. The PAHs (ranging from naphthalene to benzo[a]pyrene) were thermally desorbed from sediment samples without any pretreatment. The compounds were identified by retention times, quantitation masses, and mass spectra fit/purity and reverse fit/purity ratios. The results are reported at a 95% confidence level.

Disclaimer: The information in this document has been funded by the United States Environmental Protection Agency. The pyrolysis equipment has been provided by CDS Analytical Inc. Under assistance agreement CR# 0021-92. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Application of Thermodynamic Parameters to Gas Chromatographic Methods Development

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The use of thermodynamic parameters to predict gas chromatographic (GC) behaviour has been developed theoretically, but has not been widely applied due to a number of technical difficulties. In theory, liquid phase and compound thermodynamic parameters are transportable between columns of different physical dimensions, calculable from liquid phase and compound physical data, directly applicable to the prediction of retention times for both isothermal and temperature programmed GC in normal, multi-dimensional, or multi-chromatography applications, and potentially applicable to the verification and/or extraction of additional information from historical data.

Work in this laboratory demonstrated accurate prediction of GC retention times in temperature programmed serial GC columns (multi-chromatography), providing a means by which to "dry lab" develop multiple phase GC methods for complex environmental samples.

Work in progress includes the development of an accurate approximation algorithm for high speed calculation of temperature programmed GC retention times, the development of an assumption-free method for the experimental determination of GC column dead volumes and a cross column comparison of experimentally determined thermodynamic parameters for several common liquid phases and a limited set of target compounds.

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Expanding the Use of Passive Sampling Devices (PSDs)

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Passive sampling devices (PSDs) are small, inexpensive and easy-to-use collection devices for volatile pollutants that do not require electricity for their operation. These features have made PSDs very attractive for remote outdoor site monitoring where no power is available and for personal exposure / indoor air monitoring situations where the attributes of a small, quiet and unobtrusive monitor are particularly important. The PSDs have furnished time-weighted measurements, ranging from an eight to 168 hr duration, with good precision and accuracy for air pollutants such as ozone, the oxides of nitrogen, and sulfur dioxide.

Despite airshed modeling efforts for regulating and controlling tropospheric ozone (O_3) formation, over 70 million people currently live in U.S. counties which exceed the National Ambient Air Quality Standard (NAAQS) set for O_3 . Under the objectives of an EPA internal grant awarded in FY96, an interdisciplinary team will supplement an existing high ozone network with placement of O_3 -PSD sites at strategic gaps in the modeling grid. This PSD application is expected to provide a longer term, more highly resolved data base of regional O_3 measurements, a scenario that is not currently plausible because of economic constraints. Importantly, more attention to non-urban phenomena will be necessary now that the Clean Air Scientific Advisory Committee (CASAC) of the U.S. EPA recommended an eight-hr O_3 exposure standard replace the current one-hr standard. Interested parties are invited to concomitantly test for other O_3 -related chemical species during this aggressive two year project.

Research and Development of a Stationary Source Method for Phosgene

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Phosgene is listed as one of the hazardous air pollutants in Title I of the Clean Air Act. Phosgene is a highly toxic gas at standard temperature and pressure and has been used in military applications and for a variety of industrial uses. Although various methods have been developed for detection of phosgene in ambient air, no method is directly applicable to stationary source emissions.

The EPA has an on-going research project to develop a field ready protocol for phosgene from stationary source emissions. The results of the derivation studies, sampling train experiments and other laboratory work will be shown.

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Applications for Using Exhaled Human Breath as an Exposure Assessment Tool for Volatile Organic Compounds

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The presence of specific compounds in human blood can indicate a recent exposure (or biological response) to a drug or an environmental pollutant, or indicate a disease state of the individual. The direct measurement of blood for various substances and biomarkers is one of the primary medical diagnostic tools in current use. Because the organic constituents of exhaled human breath are representative of their blood-borne concentrations through gas exchange in the blood/breath interface in the lungs, a breath measurement could conceivably replace a direct blood measurement. A classic example of this is -the "breathalyzer" test for inebriation from ethanol.

For volatile organic compounds (VOCs), sampling and analysis of breath is preferred over direct measurement from blood samples because breath collection is non-invasive, potentially infectious waste is avoided, and the measurement of gas-phase analytes is much simpler in a gas matrix rather than a complex biological tissue like blood. To exploit these advantages for the assessment of exposure to environmental pollutants, we have developed a simple direct collection method for individual alveolar breath samples and adapted conventional gas chromatography mass spectrometry analytical methods for trace level VOCs analysis. The sampling method is based upon direct exhalation of alveolar air into a 1 liter volume stainless steel canister with an internally passivated surface. Subsequent analysis is performed in the laboratory using gas chromatography - mass spectrometry (GC-MS) methods especially modified to accommodate the high concentrations of water and carbon dioxide in breath.

The methodology has been applied to a variety of exposure situations. Specifically, we have explored exposure to environmental tobacco smoke, chloroform from chlorinated municipal water and swimming pools, vinyl chloride and 1,2-dichloroethylene from contaminated well water, various solvents and propellants in consumer products, and methyl tertiary butyl ether (MTBE), benzene and toluene from refueling of automobiles. We have measured the time dependent: elimination of VOCs through collection of series of samples

subsequent to an exposure and have e applied a multi-term exponential decay model to extract information on compartmental time constants and total dose.

Solid Adsorbent Sampling for VOC - Application in Ostrava, Czech Republic

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Seventy-nine samples were collected in an industrial city in the eastern part of the Czech Republic for VOCs. Samples were collected at two different sites: a school yard and in a residential area. Both sites were close to industrial plants with coke emissions. Samples were loaded on multiadsorbent tubes packed with 70 mg of Carboxen® 1000 (60/80 mesh) and 160 mg of Carbotrap® graphitized carbon black (20/40 mesh). The 79 samples were collected as singlets, tandems, duplicates, triplicates, and field blanks. Tubes were connected with a Teflon Swagelock union to Teflon tubing that was in turn connected to an Alpha 2 pump set at 33.0 ml/min for 60 min producing a sample volume of 2 L. Samples were taken at both sites three times a day. At one site side-by-side samples were taken in conjunction with the Ostrava Hygiene Laboratory. For shipping, tubes were wrapped in aluminum foil, sealed in a capped glass container for identification purposes, and stored in a clean paint can with activated carbon to avoid contamination. For the tube analysis, a Perkin-Elmer Automatic Thermal Desorption System (ATD 400) with a PE AutoSystem gas chromatograph FID/ECD was used. As suspected, levels of benzene and toluene were higher than other pollutants. Results for the duplicate and triplicate sample data show good correlation between the sampling tubes.

Open Path Monitoring for Trace Gases

William A. McClenny

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There are four EPA methods development objectives for FTIR-based open path monitoring systems. These objectives are:

1. Development of a guidance document to provide the basis for spectroscopic measurements of trace gases in the infrared.
2. Development of a method (TO-16) for the EPA Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air.
3. Contributions to an international consensus on acceptable performance criteria for the systems used for FTIR-based monitoring.

4. Sponsorship for the Development of a Standard Spectral Database for Infrared Spectra by the NIST.

Item 1 is now completed while items 2 & 3 are in the final stages. The item 4 has been initiated and is expected to be a topic of long term interest for the EPA.

Monitoring for VOCs in Air - Status Report

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Recent methods development efforts for volatile organic compounds in air have included:

1. The placement of one methods description TO-15 on the the AMTIC Bulletin Board maintained by the Office of Air Quality Planning and Standards and the preparation of two others, TO-16 and TO-17. TO-15 describes the use of a canister-based sampling procedure and a GC/MS analytical procedure to monitor VOCs. Method TO-16 concerns the use of FTIR-based open path monitoring and the Method TO-17 involves the use of solid adsorbents for sampling of VOCs.
2. The publication of several journal article publications in support of methods development for the North American Research Strategy for Tropospheric Ozone (NARSTO) and the Photochemical Assessment Monitoring Stations (PAMS) network. These publications show how to monitor VOCs with better sample integrity than in the past, particularly with respect to polar VOCs.
3. The publication of several journal articles on the use open path monitoring of VOCs in fence-line monitoring applications using FTIR-based systems. Emphasis has been placed on understanding and treating the generation of background spectra.
4. Evaluation of a new automated gas chromatographic system as part of the NARSTO contribution to the 1995 Southern Oxidant Study (SOS) Nashville Field Study. Diurnal patterns showing hourly updates for several biogenic compounds were seen for the first time.

Methods for Measurement of Dislodgeable Pesticide Residues in and Around the Home

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Surface residues of pesticides in residential environments present a significant exposure risk for infants and toddlers, who frequently crawl or lie on the floor and mouth their hands and other objects. Guidelines for assessing this potential exposure are mandated under Subdivision K of Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA). Both acute exposures to freshly-applied pesticide residues and chronic exposure to pesticides in house dust are of concern, although the latter may be a more important and primary route of exposure for small children.

Several monitoring devices and methods have been developed, tested, and are being standardized. A high-volume sampler capable of collecting house dust in an accurate and reproducible manner and in quantities sufficient for complex chemical analysis has been developed and already adopted as an ASTM standard. Another device rolls a pliable polyurethane foam pad over carpeted floors, lawns, and other surfaces in a manner that replicates the pressure and movement of crawling infants and toddlers in order to estimate the residues that may be picked up by the skin. Human volunteers have also been used to measure dislodgeable residues by pressing their hands on both untreated and freshly-treated carpets. A hand wipe procedure that is very acceptable to small children has been developed and field-tested. Further research and development has been undertaken in an effort to find a saliva surrogate that will provide a better means of determining the potential for residues picked up on the skin to be transferred to the mouth and ingested.

Pesticides applied to lawns may also enter the home *via* track-in on shoes and clothing, spray drift, and soil resuspension. Once inside, they can become associated with house dust and accumulate in carpets, upholstered furniture, draperies, and on household surfaces. Protected from degradation by sunlight, rain, temperature extremes, soil microbes, and wind dispersion, they may persist for years, as opposed to days or weeks on outdoor surfaces. Several small field studies have been conducted or are underway to assess the potential for transfer of lawn-applied chemical to the indoors. Controlled studies were conducted to determine the extent of track-in of lawn herbicides, insecticides, and fungicides on shoes at various times after application. Other studies have been carried out at homes where residents have applied pesticides themselves or employed commercial applicators. Multimedia monitoring was performed to determine the relative importance of the various routes of transfer (*e.g.*, track-in, spray drift) of lawn-applied pesticides to the indoors.

Several components of this research are covered, monitoring tools described, and selected findings presented.

Source Sampling Particulate Matter Research

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Research to determine procedures for measurement of emissions from stationary sources of in-stack particulate matter of aerodynamic diameter nominally 2.5 micrometer, 2.5 μ m, and smaller (PM-2.5) was performed. Interest currently exists in ambient air levels of PM-2.5. If regulation of ambient air PM-2.5 levels occurs, measurement of these emissions from stationary sources to determine their contribution to the ambient levels may be of interest also to regulatory agencies. Stationary source PM-2.5 emissions control device research is an additional potential application of this technology.

The results of this work describe a procedure using a small cyclone for performing particle sizing to determine in-stack PM-2.5. The small cyclone can be attached to existing source sampling hardware. The dimensions of the small cyclone are described. A constant sampling rate procedure is described. The procedures for obtaining the sample including determination of flow rates, actual particle size measured and other necessary measurement parameters are described. Field source sampling research will be necessary for evaluation of the procedures.

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Performance Characterizations of Laboratory and Field Technologies for Quantitation of Lead in Paints, Dusts, and Soils

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In support of the Title X mandate for the federal government to establish guidelines for lead-based paint hazard evaluation and reduction, performance evaluations are being conducted for established and new technologies.

A modular approach has been taken for development/evaluation of laboratory and field lead (Pb) measurement procedures, where analysis techniques, extraction methods, and collection methods have been evaluated sequentially.

Quantitative extraction techniques have been developed and paired with various laboratory-based and field-based analysis methods resulting in a wide array of methods with equivalent performance. Testing protocols are being developed that will predict field behavior in a laboratory setting using publicly-accessible quality assurance materials (when available).

Performance of the analytical methods are being characterized through evaluations which include the determination of bias, precision, interferences, sources of error, working range, and throughput/cost. Methods under multimedia evaluation include (1) quantitative laboratory-based methods of atomic absorption and inductively-coupled plasma atomic emission spectrometries, (2) semi-quantitative/screening field methods of portable X-ray fluorescence and test kits, and (3) the low-cost quantitative field methods of colorimetry, anodic stripping voltmetry, and reflectance. Extraction methods have included hotplate-, microwave-, and ultrasonic-based methods.

Although Pb has been the primary research focus in the medias of paint, dust, and soil, the methods selected have been developed, when possible, with multielement capability. Additionally, many of the methods have the ability to analyze Pb and other trace elements in samples from additional medias, such as ambient air, water and sediments. Performance evaluations are still needed to optimize and fully characterize these methods for multielement and other media applications.

Evaluation of the chemical composition and size distribution of individual house dust particles in a sample is being conducted by embedding scanning electron microscope (SEM) stubs into floor mats to allow SEM/XRF analysis on undisturbed housedust samples. Additionally, to better characterize dust collection techniques, a dust generation/sampler characterization system is under development that will have the ability to consistently generate test surfaces containing deposits of known dust characteristics. Five to ten size classes covering the size range of approximately 1 to 250 μm physical diameter will be used for the production of the test surfaces and characterizing the generation system's performance. Ultimately, real-world housedust dispersion is planned.

Development of Research and Standard Reference Materials (SRM) for Pb in paint and housedust is nearing completion. These materials are being developed to evaluate the accuracy of measurements being conducted. Eight materials are being produced, with the first material, powdered paint SRM 2582 (0.02% Pb), having been released for public use in 1994.

Additionally, protocols for producing method evaluation materials for paints and housedusts have been completed.

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Evaluation of Selected Multiadsorbent Tubes for Monitoring TO-14 Volatile Organic Compounds in Ambient Air

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US EPA Compendium Method TO-14, which involves collection of whole air samples in passivated canisters followed by gas chromatographic analysis, continues to be a widely used approach for monitoring volatile organic compounds in ambient air. An alternative to TO-14 has recently been developed (draft Compendium Method TO-17) by The Perkin-Elmer Corporation in cooperation with the US EPA. This new method involves pumped sampling onto sorbent tubes and analysis by thermal desorption and capillary gas chromatography.

Under contract to Supelco, Inc., RTI has evaluated two different multiadsorbent tubes for use in Method TO-17. Each tube type was tested by sampling a 39 component mixture of TO-14 compounds at a nominal concentration of 10 parts-per-billion. Compound recovery and sorbent tube breakthrough were determined for three different sample volumes and three different relative humidities. Sample analysis was performed by thermal desorption with capillary gas chromatography and flame ionization detection.

Session 6

Atmospheric Mercury Monitoring

*Cochairs: Robert K. Stevens, U.S. EPA, Research Triangle Park, NC;
and Thomas D. Atkeson, Florida DEP, Tallahassee, FL*

Overview of the South Florida Atmospheric Mercury Monitoring Pilot Study

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In 1989, elevated levels of mercury were discovered in Florida freshwater fish—resulting in an unprecedented issuance of health advisories to Florida fishermen. After extensive monitoring, approximately two million acres of Florida surface waters - over half the fresh waters of the state - are now subject to bans or restrictions on consumption of several species of fish. The most severe problem is located in south Florida, where the entirety of the Florida Everglades is covered by consumption bans. To begin to assess the potential significance of atmospheric deposition of mercury to Florida's water bodies and watersheds, in 1991 the Florida Department of Environmental Protection initiated the Florida Atmospheric Mercury Study (FAMS) to quantify the temporal and spatial variability in atmospheric deposition across Florida. At the present time insufficient data is available to make responsible conclusions on sources of Hg measured at the FAMS sites. The FAMS system design has served to assess the spatial and temporal trends in deposition. The long integration periods used by FAMS are not ideal for determining the mechanisms that distribute mercury from local, regional or global sources. In 1995 the US Environmental Protection Agency and the Florida Department of Environmental Protection along with Florida State University, the University of Michigan, the Electric Power Research Institute, and Florida Power and Light designed a field air quality monitoring and modeling study that was implemented in south Florida in August and September of 1995. The principle objectives of this pilot study were to obtain wind flow patterns, source and ambient chemical composition data to evaluate the ability of source and receptor models to determine the transport mechanisms of Hg to the Everglades. This presentation will expand on the rationale for this study and the studies implication to our understanding of the fate and transport of Hg to Eco-systems.

Preliminary Phase of Vapor Phase Mercury Measurements Made During the SUAMP Project

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Total vapor phase mercury (Hg) measurements were made continuously at five sampling sites for a one month period as part of the South Florida Urban Atmospheric Mercury Project (SUAMP). The primary objectives of the SUAMP project are to quantify the atmospheric contribution of the Hg loading to South Florida (Dade and Broward Counties) and to investigate the importance of Hg emissions from local urban sources relative to the regional anthropogenic and global sources. The field study portion of this project took place from August 6 to September 6, 1995. Total vapor phase Hg measurements were made at five sites utilizing two collection methods: integrated 12-hour samples using Au-coated glass bead traps and continuous measurements using automated Hg vapor analyzers. Co-located measurements compared very well, with agreement between the two methods determined to be less than six percent. Monthly-integrated mean concentrations at the five sites ranged from 1.3 to 4.0 ng/m³. Although this is a considerable range in the monthly mean concentrations, daily site to site variations were found to be even greater. In some instances, there were periods (1-2 hours) during which vapor phase Hg concentrations at individual sites exceeded 15 ng/m³, with maximums reaching 50 ng/m³. A preliminary analysis of this data set including a limited evaluation with surface meteorological data will be presented.

Atmospheric Deposition of Mercury in South Florida: Preliminary Results from the SUAMP Project

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Event precipitation samples were collected concurrently at seventeen sampling sites for a one month period as part of the South Florida Urban Atmospheric Mercury Project (SUAMP). A primary objective of the project is to determine the magnitude of the atmospheric contribution to the Hg loading to South Florida, specifically to Dade and Broward Counties. The measurement campaign took place from August 6 to September 6, 1995. Daily event precipitation samples were collected each morning at each site, with several sites being visited twice daily (morning and evening). Hg concentrations ranged from 5 to 110 ng/L in event precipitation samples collected at the seventeen sites. Volume-weighted mean concentrations at each of the sites for the one month study period

ranged from 13 to 31 ng/L. Although these monthly means reflect a significant range in concentration, a more dramatic spatial pattern was evident in the daily event concentration field. In addition, there are significant differences between events at each individual site over the one month study period. This paper includes a preliminary evaluation of the Hg in precipitation measurements.

Dry Deposition of Mercury in South Florida: Preliminary Results

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Measurements of the dry deposition of mercury (Hg) were performed daily at several sampling sites for a one month period during summer 1995 as part of the South Florida Urban Atmospheric Mercury Project (SUAMP). A primary objective of the SUAMP project is to determine the magnitude of the atmospheric contribution to the Hg loading to South Florida (Dade and Broward Counties). Twelve-hour integrated samples were collected for periods ending 0800 and 2000 EDT each day, using a dual surrogate surface approach. A newly designed and tested aerodynamic water surface was utilized in tandem with a well-characterized symmetric low-speed airfoil (Frisbee-shaped). This latter deposition plate was uniformly coated with Apiezon L grease and fit tightly into the top of the airfoil. The newly designed collector replaced the greased deposition plate with a circular water collection surface. Vapor and particulate Hg samples taken concurrently with the dry deposition samples are used to apportion the dry deposition by phase and species. A significant day-to-day variation in the Hg deposition was observed at the sites. This paper includes a preliminary evaluation of the Hg dry deposition measurements. Trace elements measured concurrently with the Hg on the surrogate surfaces will be utilized to evaluate the methods for atmospheric Hg and to aid in diagnosing the sources of the dry deposition.

Methods to Measure Atmospheric Mercury in South Florida

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As part of the South Florida Mercury Monitoring and Modeling Pilot Study (SOFAMS), we collected replicate samples at two sites using all of the various sampling methodologies which have been recently employed to study gaseous Hg, aerosol Hg, and rainfall Hg. Sampling protocols developed by the research group conducting the Florida Atmospheric Mercury Study (FAMS) were used to collect 24-hour integrated rainfall, aerosol, and total gaseous Hg (TGM) sampling at the Davie/UF-IFAS station and the FAMS Andytown tower site approx. 1 mile southwest of Highway 27—Griffin Road intersection. In addition, 48-hour integrated Reactive Gaseous Mercury (RGM) samples were collected at both sites using the ion-exchange filter pack technique being developed by Nicolas Bloom at Frontier Geosciences, Seattle. The University of Michigan group collected 12-hour integrated samples at the Davie site, and 24-hour integrated samples at the Andytown site using similar sampling techniques for rainfall, aerosols, and TGM. In addition, TGM was measured using a Tekran continuous TGM analyzer at the Davie site, and a "surrogate surface" technique was used to collect RGM at the Davie site. The goal of this work was to provide direct intercomparison between the sampling and analytical techniques used by the FAMS and Michigan groups, as well as to link the long-term FAMS data set to the data generated during the SOFAMS experiment, and future extensions of this experiment in south Florida.

Atmospheric Transport, Transformation, and Deposition of Mercury in Florida

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A five year study focusing on the atmospheric deposition of Hg in north, central, and south Florida has been operational since May, 1992. One of the primary objectives of the Florida Atmospheric Mercury Study (FAMS) is to quantify the seasonal and geographical variations in Hg deposition. Precipitation, aerosol, and gaseous Hg samples have been collected at nine sites throughout Florida for periods ranging from 3-36 months. The summertime wet season in south Florida accounts for 80-90% of the annual rainfall Hg deposition. Deposition rates in south Florida are 30-50% higher than those from north and central Florida. These rates are dependent upon increases in rainfall Hg concentration during the summer as well as increases in summertime precipitation. We are currently evaluating the marine background Hg contribution to Florida, the possibility of transport from other regions, and the speciation and transformation of the Hg found in precipitation.

Meteorological Flow Regimes Influencing Atmospheric Concentrations and Deposition During the 1995 SUAMP

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The problem of atmospheric mercury source attribution for the Everglades and the rest of South Florida is complicated by the complex wind flow and precipitation patterns observed across this region. As a result, one goal of the 1995 South Florida Urban Atmospheric Mercury Project (SUAMP) has been to adequately define the actual three-dimensional wind flow and precipitation patterns that occurred during the project period. Definition of these fields will allow for the establishment of empirical relationships with observed mercury concentration and deposition patterns in an effort to promote a scientifically credible source attribution of atmospheric mercury deposition through the use of hybrid-receptor-based modeling.

In support of these efforts, the meteorological observations routinely made by the National Weather Service (NWS) were supplemented with additional surface and upper air meteorological measurements across the study domain. Analysis of this data shows that during the 1995 Field Study, three dominant meteorological flow regimes were observed: local land-/sea-breeze circulations, southeasterly synoptic flow related to the semi-permanent Bermuda High and southwesterly synoptic flow in the wake of Tropical Storm Jerry. This paper presents the results of this analysis and discusses preliminary efforts to model these flows and their potential impacts on atmospheric mercury concentrations and deposition patterns across South Florida.

Source Characterization in Support of Modeling the Transport of Mercury Emissions in South Florida

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Source characterization is an essential component used to model the impact

of stationary source emissions on selected receptor sites. In the SOFMMS, source profiles and emission rates for Hg, trace metals, carbon, and SO₂ were obtained from a resource recovery incinerator, a medical waste incinerator and a coal fired cement kiln operation. The source profiles contain the concentrations of particulate mass, trace metal compositions including Hg and SO₂ present in the emissions. Emission rates for SO₂ and particulate matter were also obtained from these three sources during the period between August 5 and September 1, 1995. A recently developed Teflon coated dilution sampling system was used to obtain the source profiles from the three sources. The dilution sampler was designed to remove 1 liter/minute from the stack emissions and dilute the sample with clean nitrogen. Residence time in the dilution system prior to collecting samples was approximately 20 seconds. This was sufficient time for the hot gaseous emissions to condense and or coagulate to particles which were collected for subsequent analysis. A differential optical absorption spectrometer was also used at the resource recovery incinerator to continuously measure the Hg⁰ and SO₂ concentrations in the stack emissions. This instrument measures these emissions across an open path in the stack. EPA Method 29 was used to measure Hg⁰ and water soluble Hg (ie. ionic Hg⁺⁺) emissions for all three sources. This presentation will describe the equipment and methodology used to characterize the source emissions. The ratios of Hg⁰ to total Hg emissions for these three types of stationary sources was also determined with EPA Method 29 and with gold coated glass beads coupled to the dilution sampling system. The variability of the stack gas emissions and source profiles will be presented.

The information in this document has been funded wholly or in part 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.

Receptor Modeling of Atmospheric Mercury in South Florida: Preliminary Results

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The South Florida Atmospheric Mercury Measurement and Modeling Pilot Study was conducted in August 1995. An objective of the study was to determine whether receptor modeling methods could be used to apportion atmospheric mercury among three known point sources; a municipal waste incinerator, a medical waste incinerator and a coal fired cement kiln. Source signatures were obtained at each facility over several days while integrated 12 hour ambient samples were continuously collected during the entire month at four receptor sites located in Dade and Broward counties. A fifth background site was located

on Adams Key off Florida's east coast. Teflon and quartz filter packs were used to collect fine fraction particulate samples at all source and ambient sites while annular denuders were used to collect inorganic gases. Measurements for SO₂, HCl, HNO₃, mass, elemental and volatile carbon and trace elements were obtained. Gold coated beads were used for collection of vapor phase mercury and analyzed by cold vapor atomic fluorescence. EPA Method 29 was also employed at the sources to determine Hg⁰ and Hg⁺² emissions. Variations of the source emissions observed for different days provided information on uncertainties associated with these signatures. Initial receptor modeling results using chemical mass balance techniques (CMB7) will be presented for several days with varying meteorological conditions.

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DOAS Measurements of Elemental Mercury and Sulfur Dioxide from a Resource Recovery Incinerator

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An OPSIS, Inc. Differential Optical Absorption Spectrometer (DOAS) was installed on one of the two emission stacks of a resource recovery municipal incinerator in South Florida. The setup included an ultraviolet light-source and a receiver, monitoring across the 7' stack. The DOAS spectrometer was located in an air conditioned shelter at the bottom of the stack. The optical signal was guided through a 160' quartz fiber to the instrumented shelter. The DOAS instrument was set to monitor sulfur dioxide and mercury sequentially with a 2-minute cycle time. Sulfur dioxide (SO₂) and elemental Hg⁰ were measured for a period of 30 days between August and September 1995. These measurements were made as part of the South Florida Mercury Atmospheric Monitoring Modeling Study (SOFAMMS). The objectives of the SOFAMMS were to obtain source and ambient chemical data to evaluate source and receptor models to assess the impact of stationary source emissions on downwind receptor sites. The DOAS measurements were used to assist in the speciation of total Hg emissions being emitted by incinerators. This speciation was performed by comparing the DOAS Hg⁰ measurements with measurements made from impinger samples (EPA Method 29) collected during the same time period. The measured results for elemental mercury were in the range of 0-60 ug/m³, and averaged 13 ug/m³ during the measurement period. The measured data for sulfur dioxide was in the 0-600 mg/m³ range, and averaged 130 mg/m³. This paper will present details of DOAS measurement methodology and describe the statistical comparisons of Hg⁰ data obtained with the DOAS and Method 29.

Session 7

Ambient Air Measurements

Chair: Suresh Santanam, Sterns and Wheler, Cazenovia, NY

Effect of Acidity on the Sampling and Analysis of Carbonyls Using DNPH Derivatization Method

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Determination of carbonyl compounds in ambient air as well as in industrial stacks receiving increased attention because of the critical role these compounds play in tropospheric organic chemistry. Aldehydes and ketones are stamped using DNPH derivatization methods (EPA 001, TO-11, and CARB 430) followed by HPLC/UV analysis. The acid catalyzed chemistry associated with the reversible derivatization reaction is complex and may lead to ambiguous results. In this investigation we present sampling efficiencies, stability of sampled carbonyl hydrazones and recoveries at different pH conditions. Optimum acidic conditions required for carbonyl monitoring using various methods are discussed.

Airborne Hexavalent Chromium in Southwestern Ontario

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This study reports the first field measurements of airborne hexavalent chromium (Cr(vi)) in southwestern Ontario. Hexavalent chromium has been identified as an inhalation carcinogen, but questions such as how much of the routinely monitored airborne chromium (Cr) is in this oxidation state; how much Cr(vi) are we being exposed to; and how much is in the aerodynamic size fraction necessary for it to be classified as an inhalable particulate still remain to be answered. The sampling and analytical methodology for detecting airborne Cr(vi) at concentrations less than 1 hg/m^3 (nanograms per cubic metre) was developed in the mid 1980s. Hexavalent chromium was identified as an air toxic of concern for the 1991/93 Windsor (Ontario) Air Quality Study and a small pilot study addressing this contaminant was conducted during the summer of 1992. The results of this study indicated that approximately 20% of the routinely monitored airborne chromium was in the hexavalent form. In addition, the risk assessment undertaken on these data found that the range of carcinogenic health risks attributable to airborne Cr(vi) were between 1.4×10^{-6} and 3.0×10^{-4} for

people living in the Windsor area. During the next summer, analyses of concurrent indoor and outdoor 24-hour air quality samples taken at 33 different residences in Hamilton (Ontario) resulted in geometric mean Cr(vi) concentrations of 0.20 hg/m^3 and 0.55 hg/m^3 respectively. Again, the airborne concentrations of Cr(vi) were found to be 20 to 25% of the total Cr. During the summer of 1994, an airborne Cr(vi) size-fractionation study was conducted in Hamilton. From analyses of these data, the majority of the Cr(vi) was found to be less than 10 μm (microns) in aerodynamic diameter. Collectively, these findings indicate that outdoor airborne concentrations of Cr(vi) are approximately 20 to 25% of the total airborne Cr; that indoor airborne concentrations of Cr(vi) bear little or no relationship to and are less than half of those measured outdoors; and that the majority of the airborne Cr(vi) measured by this new methodology is in the inhalable fraction.

Monitoring Reformulated Gasoline in Milwaukee, Wisconsin

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Beginning in January 1995, the 1990 Clean Air Act Amendments required the introduction of *reformulated gasolines* (RFG) in six counties in southeastern Wisconsin. The reformulated gasoline was to contain an increased percentage of chemical oxygen (oxygenates); to contain reduced toxic components; and to provide lower evaporative emissions. With introduction of the oxygenated gasoline blends, the Wisconsin Department of Natural Resources (DNR) began receiving numerous citizen complaints. Complaints expressed concerns about damage to internal combustion engines, reduced automotive performance, and health effects of the reformulated gasoline. Because of questions about health effects, along with a lack of information on exposure to urban populations, the DNR was asked to immediately initiate an air monitoring study. This paper will report on how the monitoring study was conducted and the results of the study.

Volatilization and Dispersion Measurements for Airborne Methyl Bromide Downwind of a Treated Agricultural Field

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A field study was conducted of methyl bromide volatilization flux, dispersion, and atmospheric fate. Air concentrations of methyl bromide were measured above a fumigated field and downwind from the field with the objective of comparing vertical flux with horizontal flux based upon measured methyl

bromide concentration and meteorological data. Another objective was to compare downwind air concentration data to concentrations predicted by a dispersion model (Industrial Source Complex-Short Term II [ISC-STII] model) to begin the process of identifying potential methyl bromide sinks. Flux, vertical profile, and single-height air concentrations were measured at four different locations extending from the center of the treated field to nearly 0.8 km downwind. These concentrations were used to determine air concentration profiles and downwind dispersion concentrations. The dispersion values were compared with those generated from the ISC-STII Model. This study showed (1) Horizontal flux near the downwind edge was 102% of mid-field vertical flux; (2) Vertical air concentration and flux profiles farther downwind showed depletion of methyl bromide near the surface of an adjoining mature strawberry field. Absorbed methyl bromide was found in the soil surface of the same field; and (3) Methyl bromide air concentrations measured downwind of the treated field source were in agreement with those predicted by ISC-STII model, allowing the construction of downwind isopleths for each day of sampling. Downwind concentration modeling of this type will be useful for estimating human exposure and also for setting buffer zones for treated fields.

Ambient Trends of Benzene in California From 1990 Through 1995

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The Air Resources Board (ARB) has for the past six years maintained a routine, canister based toxics monitoring network in urban areas of California. The record is now extensive enough to evaluate for trends in toxic pollutants within the State. This paper evaluates the trend in benzene at over 20 different sites in major population centers in California between 1990 and 1995. Including measurement variability, a significant downward trend has been observed throughout the State with reductions frequently approaching fifty percent. The paper also presents emissions inventory of benzene for the same period whose reductions can be attributed to the vehicle control and clean fuel programs.

Air Pollution from Cookstoves in Developing Countries: Results from A Field Study in China

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Cookstoves in developing countries are individually small, but so numerous that they could influence global inventories of greenhouse gases. As part of a USEPA/East-West Center cooperative project, which has been primarily aimed at studying greenhouse gases from widely used small-scale combustion devices, emissions from 28 types of fuel/stove combinations commonly used in China were measured for carbon dioxide, products of incomplete combustion (PICs, e.g., carbon monoxide, methane, hydrocarbons, particulate matter), NO_x, SO₂, etc. Since many of emitted pollutants have adverse health effects, and they could cause elevated concentrations in homes, results from these measurements also enable us to assess health risks from these cookstoves.

It was found that burning biomass fuels generated greater emission factors of PICs than burning fossil fuels, and that increasing stove efficiencies did not necessarily lead to a reduction in emissions of PICs. PICs can be considered as an indicator of health risk. In addition, because of their great relative indices of greenhouse effect, contributions from PICs were found to be significant, sometimes close to or even greater than those from CO₂. This suggests that biomass fuel cycles are not necessarily green-house neutral even when the fuel is harvested on a complete renewable basis.

Size Spectra and Sources of Elemental Constituents of the Baltimore Urban Plume

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Micro-orifice and rotary impactors were used to collect size-segregated aerosol samples spanning the range <0.05 μm to >150 μm at five sites near Baltimore, MD, during a 20 day period during August, 1995, as part of the U.S. EPA Great Waters Program. Samples were collected on the roof of the Eastern

Avenue Fire Station in downtown Baltimore, on a pier at Hart-Miller Island (15 km south-west of Baltimore), onboard the research vessel Anderson (located on the Chesapeake Bay), and at the Still Pond Coast Guard Station on Maryland's eastern shore. Background samples were collected upwind from Baltimore at the University of Maryland's Baltimore Campus located 15km west of Baltimore city. Samples were analyzed for up to 45 elements, including V, S, Zn, Sb, As, Br, Mg, Mn, K, Na, I, Cd, Cu, Nd, Sm, Yb, U, by x-ray fluorescence (XRF) and instrumental neutron activation analysis (INAA), for total carbon by light transmission, and for particulate mass by gravimetry. Used in conjunction with a numerical model, the complete aerosol composition vs. size distributions were used to characterize dry deposition to Bay waters both by size and by source.

Session 8

Tropospheric Ozone Measurement

Chair: Carmo Fernandez, Arizona DEQ, Phoenix, AZ

Voluntary Emissions Reduction Efforts During the Summer of 1995 in Wisconsin

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Many areas of the United States which do not meet the USEPA standard set for tropospheric (ground-level) ozone are implementing voluntary emissions reduction efforts to reduce emissions which lead to the formation of ground-level ozone. The hope is that, through voluntary efforts, enough ozone-forming emissions will be forgone to reduce the peak ozone concentration of a forecasted high ozone day. Aside from reaching attainment of the ozone standard in a regulatory vein, public health and welfare would benefit from improved air quality. The states of the Lake Michigan basin have developed a common effort known as Ozone Action! Day (OAD). This paper will document the OAD experiences of Wisconsin in its inaugural season of participation in this regional effort that occurred in the summer of 1995. These experiences included an official kickoff day prior to the start of summer, regional forecasting efforts, media notification, development of a network of employers who desired individual notification, and other quasi-governmental participation. Specific suggestions for public participation are also included in this paper, along with results of surveys of public acceptance of the OAD message and efforts.

Paso del Norte Pilot Border Study of Ozone Precursors and Air Toxics

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The Paso del Norte area (El Paso, Texas, Ciudad Juarez, Chihuahua, and Sunland Park, New Mexico) currently experiences ozone concentrations that exceed the National Ambient Air Quality Standard for ozone. In addition,

concerns have been raised about the nature and quantity of toxic air pollutants in the area. A comprehensive monitoring program for ozone precursors and air toxics in the Paso del Norte border area is planned by the U.S. EPA for the summer of 1996. A pilot study was carried out in October 1995 in this area to test the appropriateness of proposed sampling and analysis methods and to provide preliminary data to be used in planning for the Summer 1996 study. Two monitoring sites were selected, one in Ciudad Juarez, and the other in the El Paso area. The sampling was carried out every second day from October 21 to October 29, from 0300 to 0900 hr. The air samples were collected using stainless steel canisters (for VOC in the C_2 - C_{12} range), Tenax-TA solid adsorbent cartridges (for C_8 - C_{20} hydrocarbons), DNPH impregnated C_{18} Sep-Pack Cartridges (for carbonyl compounds) and Teflon impregnated glass fiber filters followed by PUF/XAD/PUF "sandwich" cartridges (for SVOC). The data set obtained from the analyses of these samples will be presented and the implications for the upcoming 1996 study will be discussed.

Overview of the ISO 14000 Environmental Management Standards

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In 1996, the International Organization for Standardization (ISO) will publish the first of a series of international standards addressing environmental management. The emerging ISO 14000 environmental management standards pose a potentially greater impact on the world community than the ISO 9000/10000 standards that preceded them. Like quality, environmental management cuts across all business sectors; however, unlike quality, environmental issues include regulatory aspects, diverse public interest groups, and an arguably broader scope of applications.

Initially, 18 standards have been proposed to encompass environmental management systems (EMS), environmental auditing (EA), environmental labeling (EL), environmental performance evaluation (EPE), and life-cycle assessment (LCA). Five standards have reached the stage of draft international standard (DIS) and two of these are the proposed EMS standards, ISO 14001 and ISO 14004.

This paper provides a general overview of the ISO 14000 standards, including their contents and their role in the overall ISO 14000 series. This paper will also briefly contrast these standards with the ISO 9000 quality management standards currently in use.

Session 9

Particle Exposure

Chair: Robert M. Burton, U.S. EPA, Research Triangle Park, NC

Characterization of Episodic Air Pollution Study

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In recent epidemiological studies adverse health effects have been associated with increased levels of air pollution. The causal relation between the airborne stressor and the health effect endpoint is still a matter of debate. The assessment of exposure to possible stressors is currently lacking from a sufficiently detailed phenomenological description of air pollutants in cities.

A descriptive study was carried out to better understand the behavior and sources of a number of air pollutants, in particular fine suspended particulate matter. At an urban site, located down-town Amsterdam, and a rural site, Biddinghuizen 50 km north-east of Amsterdam pollution levels were monitored during the winter of 1993-1994.

Increased levels of particulate matter were observed under the following conditions: New Year's Eve, with very high but short-lived concentrations; high wind speeds, causing resuspension of settled dust; and stagnant weather conditions, with low rates of pollutant transport.

During winter-smog episodes the contribution of submicron particles ($<1 \mu\text{m}$) to PM₁₀ was found to increase from 10 to 20% whereas the contribution of the fine mode ($<2.5 \mu\text{m}$) did not increase significantly. The contribution of secondary aerosol definitively increased during stagnant weather conditions (over 70%), clearly dominating the observed PM₁₀ levels. The contribution of soot increased only marginally.

PM₁ levels and compounds emitted by mobile sources (like benzene, CO and aldehydes) showed a good correlation suggesting that traffic is the main source for PM₁ in cities. No good correlation was observed for PM₁₀ and these traffic-related compounds. Principal component analysis revealed sources related to emissions of mobile source and confirmed the dominating contribution of traffic-related particulate matter to PM₁. These findings infer that decreasing traffic-intensity does not substantially reduce PM₁₀ levels.

The results of this study improved the understanding of the behavior and occurrence of air pollutants in cities. However, the fact that no real episode occurred during the project period leaves the question on the composition and levels of air pollutants during real winter-smog episodes as defined by current regulations. Hence further research will be required in the coming winter periods

hoping that such episodes will occur for the sake of research. However, until now only the New Year's Eve episode has proven to be punctual.

Policy and Science on PM in the Netherlands, Bridging the Gap

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In quite a number of countries with different climates and cultures epidemiological studies have reported associations between daily concentrations of particles and adverse health effects. In terms of protecting public health it would be imprudent not to regard the demonstrated associations as causal, however there still remain questions on the toxicological mechanisms and the fraction of the air pollution that may be held responsible for the effects. In this twilight zone of science and policy a project is described, which is set up to give the Dutch policy makers some guidance on the risk management of PM.

As health problems can be demonstrated at levels below the current PM standards and a threshold which is to be deemed safe cannot yet be established, a simple tightening of existing standards doesn't seem to offer the solution, even if such a measure would be economically viable. A second complicating factor is that PM is not just one simple component but it is a mixture of a number of different substances. For the moment even the conjecture that PM may be a proxy for the total air pollution mixture cannot be dismissed on the basis of the epidemiological data. For these reasons a different approach is chosen in the project to bridge the gap between policy and science.

This approach is based on a further disentanglement of the main components of PM. In order to discover the sources of these main components of particulate matter and to find out which processes determine the ambient concentrations of these components, the air quality is one of the trails that is explored. The other trail is formed by the quantitative assessment of health risks, in order to assess the extent of the health risks of these components of PM. When this information from both of the trails is combined with the results for the different policy scenarios it will be possible to offer the policy makers a choice of different alternatives and the health risks that may be associated with these alternatives. The choices a government has to make for the risk management of the PM problem may then be taken with some scientific guidance.

As a matter of simplification PM will be classified in five broad categories based on the particle sizes and chemical speciation: PM₁₀, PM_{2.5}, PM_{0.1}, carbonaceous and secondary aerosol. The emissions and phenomenology of these five parts of the pentagon of PM will be established for the Netherlands.

With an adequate dispersion model the concentrations for different policy options and abatement strategies will be calculated for an averaging period of one year and for the situation of a typical air pollution episode in the Netherlands. The different results of these alternatives may then be used by policy makers as a basis for their decision making.

The important gain from such an approach is that it enables you to see in advance if for instance a strategy of abatement of sources of PM has a similar or different result for the levels of e.g. PM_{0.1} or carbonaceous aerosol. In this period when the exact culprits are not yet known, following a non regret policy wich has effects on a number of PM components at the same time may be a cost effective way of progressing.

Influence of Weather on Aerosol Exposure in Selected, Highly Populated Metropolitan Areas of the United States

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Particle research conducted under the EPA/Harvard Five City Exposure Study has included both realtime continuous and integrated 24-hour measurements of particulate and meteorological components. Analysis of data indicates both direct and indirect associations between temperature, humidity and the physical and chemical make-up of particles. Field studies conducted in Philadelphia, Pittsburgh, Washington, DC, and Nashville suggest correlation between ambient fine particles (PM_{2.5}) concentrations and delta T, the absolute value of the difference between the average daily temperature and the average indoor temperature of 68 F. Conversely, coarse particle concentrations (PM_{2.5} - PM₁₀) do not correlate well with temperature components but are related more to wind speed and local activity.

Other particle measurements suggest that the high summer temperatures simultaneously drive more of the aloft, regionally transported sulfates down to ground level, while at the same time use the increased vertical mixing to flush out a significant amount of the ground level, locally generated components such as soot and organics.

Continuous fine particle mass, determined simultaneously from realtime particle sizing measurements and from heated filter continuous mass measurements, reveal significant differences when the ambient relative humidity is above the fifty percent level. These differences indicate that the hygroscopic mixed-salt aerosol is constantly absorbing or releasing water as the humidity varies above

the delinquescence point for the aerosol.

These dynamic properties which have a profound effect on the characteristics of the aerosol in which populations of large metropolitan areas are exposed. Choosing the proper aerosol that components for use in health effects exposure studies should be carefully considered.

The Role of Total Human Exposure Measurements of Particulate Matter in Community Epidemiological Studies

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Measurements of total human exposure are possible for cohort studies covering a few individuals for a short time. However, many epidemiological studies of particulate matter (PM) use community-based rather than cohort data, e.g. deaths in a large city or emissions to a hospital serving a large metropolitan area over periods of one to several years. For such studies an indicator of average, daily community exposure must be used. Typically this is obtained from measurements of PM concentration at one central site. It will be shown that such epidemiological studies relate health outcomes to exposure to ambient particles not to exposure to total particles. Exposure to ambient particles occur both when people are outdoors and when people are indoors or in other microenvironments. Epidemiological studies using community exposure data do not provide information on the potential health effects of particles generated indoors or particles due to a person's presence or activities (personal cloud). Therefore, measurements of total human exposure are not useful for community epidemiological studies (unless the individuals constitute the cohort and their individual total human exposure is measure for the duration of the study). However, total human exposure studies may be useful if they help us understand what fraction of ambient particles are found indoors and what parameters influence that fraction. Examples of how concepts from total human exposure research can be used to improve estimates of community exposure to ambient PM, as well as further research needed in this area, will be discussed. The importance of distinguishing fine mode from coarse mode PM and for measuring specific species in both the fine and coarse modes will be emphasized.

A Synoptic Climatology of Fine Particle Acid Aerosols

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High concentrations of ambient, strong aerosol acidity (H^+) were measured

during the summer of 1990 at Uniontown, Pennsylvania. The synoptic climatology of the region was investigated for clues to the meteorological conditions that were associated with the temporal variability of the H^+ concentrations, with particular emphasis on the conditions conducive to high concentrations of acid aerosols. Since H^+ is a secondary pollutant, formed primarily through oxidation of sulfur dioxide (SO_2), transport of pollutant precursors from their source regions is an important factor in determining the magnitude of the H^+ concentrations. Local meteorological factors such as temperature, wind, and the height of the mixed layer were also important for determining the variability in H^+ concentrations. This research shows that both local meteorology and regional circulation contributed to episodic events of ambient H^+ . Analyses of the meteorological parameters affecting ambient concentrations of acid aerosols should at least include the temperature, dew point (or some other indicator of atmospheric moisture), mixing height, and the wind speed and direction at the surface and for an upper level of the atmosphere that facilitates the regional transport of pollutants.

Assessment of the Temporal Relationship Between Summertime Ultra-Fine Particulate Count Concentration With PM in Washington D.C.

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Recent epidemiological evidence has shown a significant relationship between ambient daily particulate mass concentrations and human health effects as measured by cardio-pulmonary morbidity and mortality. Most of the research aimed at determining causal agents focuses on the combustion-related component of PM₁₀. Some studies have suggested that ultra-fine aerosols may be important factor, either by their count concentration or by other mechanisms. The temporal relationship between mass (PM_{2.5} and PM₁₀) and ultra-fine particles (mass and number concentration) was characterized by making daily and hourly measurements of size classified particles between .02 and 10.0 μ m, PM_{2.5}, and PM₁₀ during the summer of 1994 in Washington, DC. Particles smaller than 0.7 μ m aerodynamic diameter were measured with a TSI model 3934L scanning mobility particle sizer, and a TSI model 3310A laser-Doppler velocimeter was used for particles between 0.7 and 10 μ m. Two TEOM continuous mass analyzers were used to measure hourly PM_{2.5} and PM₁₀ in conjunction with integrated 24 hour low-volume PM samplers. The temporal relationship between hourly and daily means of particle count, surface area, and volume concentration in different size ranges and collocated measurements of PM_{2.5} and PM₁₀ is presented. Preliminary analysis shows no correlation ($r=.00$) between daily (mean 24 hour) particle number concentration or ultra-fine mass

and PM_{2.5} or PM₁₀. This is consistent with the lack of temporal variability (on a daily basis), local sources, and short (+1 day) lifetimes of ultrafine particles compared to the sources (regional transport) and lifetimes (many days) of the larger particles (0.4 to 1 μ m) that dominate the fine PM concentration. If the lack of an association between count and mass concentration holds over other seasons and locations, this may make it more difficult to postulate theories of mechanisms for PM health effects which rely on a temporal association between particle counts or ultra-fine mass and measures of PM_{2.5} or PM₁₀.

The Relationship Among TSP, PM₁₀, PM_{2.5}, and Inorganic Constituents of Atmospheric Particulate Matter at Multiple Canadian Locations

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Abstract not available.

Relationships Between Daily CoH, Visibility Measurements and Fine Mass Concentrations in Philadelphia, PA

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A major limitation in the evaluation of the health effects of fine particulate matter has been the fact that fine particle mass (PM_{2.5}) measurements are not historically available. However, the recent Harvard Metropolitan Acid Aerosol Characterization Study (MAACS) provides comprehensive PM data at multiple sites in Philadelphia, PA that are useful in determining quantitative relationships between PM_{2.5} and the historically available Coefficient of Haze (CoH) and visibility records, which have been collected daily for decades in that city. These latter two measures are useful metrics of submicron primary and secondary aerosols, respectively. Thus, these two measures can provide a basis for predicting historical daily PM_{2.5} concentrations. In this work, we present predictive models for PM_{2.5} based upon daily measurements of both CoH and visibility (corrected for RH) made in Philadelphia, PA during the years 1992-1993, when the comprehensive MAACS PM_{2.5} are also available. These predictive equations will be especially useful in that they will allow time-series evaluations assessing the role of PM_{2.5} in historical TSP-mortality relationships previously reported for Philadelphia, PA.

Atmospheric Mass and Metal Size Distributions Measured Around Lake Michigan

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Numerous atmospheric mass and metal size distributions (0.15-100 μm) were measured in Chicago, IL, in South Haven, MI, in Sleeping Bear Dunes, MI, and over Lake Michigan since 1989. Cascade and Moudi impactor were used to determine the size distribution in the fine particles ($<2.5 \mu\text{m}$), while Noll Rotary Impactor (NRI) was used to collect coarse particles ($>2.5 \mu\text{m}$). The mass size distributions generally followed a bi-modal pattern, with peaks in the 0.1-1 (fine particle mode) and 20-30 μm range (coarse particle mode). The anthropogenic metals generally followed a bi-modal distribution with peaks in the 0.1-1 μm range, and the 8-10 μm range. Calcium and sodium peaked around 8-10 μm , while magnesium generally peaked in the 10-20 μm size range. Size distributions of iron demonstrated considerable variation between samples. The iron mass peak was generally in the 1-12 μm range.

Quality Control and Reference Equivalency of PM Monitoring Systems

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Systematic air pollution measurements are performed for two purposes, viz. to check for compliance with air quality directives, and to support rule making. An appropriate quality of the systematic measurements can be ensured as follows.

Firstly, the measurements will have to be performed following the general requirements laid down in EN45001 (general criteria for the operation of testing laboratories). Basically, a certified quality control system according to EN45001 aims at appropriate product quality, fixed modes of operation, traceability, and reproducibility.

Secondly, an appropriate reference method will have to be available to harmonize the monitoring methodology.

The European Union (EU) has adopted the following strategy to improve the so-called PM₁₀ monitoring methodology:

- An appropriate reference method has been designated by convention to harmonize the SPM monitoring methodology in the EU for the thoracic particles (ISO7708, 1995).

- EU Member States will have to use either the reference method under routine conditions, or methods which are equivalent to the reference method (equivalence methods), for the survey of ambient air quality.
- EU Member States will have to take the necessary steps to ensure that equivalence methods are tested by an appropriate reference equivalence procedure.

Following these recommendations, the EU has supported the work done by CEN (European Committee for Standardization) to harmonize the performance of sampling instruments for compliance monitoring:

- Drafting a field test procedure to demonstrate equivalence of sampling methods for thoracic particles, with a reference sampling method for the thoracic fraction of SPM;
- Validating and assessing the practicability of the designated reference equivalence procedure by trying it out in demonstrative field tests at characteristic measurement locations in the EU.

This presentation aims to elucidate the CEN/EU reference equivalence procedure for PM₁₀, and the pertinent EN45001 quality systems approach.

Application of Near-Field Optical Techniques to Ambient Particulate Matter: Physical and Chemical Structures

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In the past few years, new frontiers in materials research have been opened through the development of the near-field scanning optical microscope, or NSOM. The NSOM modifies standard optical techniques by increasing spatial resolution through the use of geometry to confine the optical field. The application of NSOM to particulate analysis will be discussed. Though many techniques are able to look at a distribution of samples, i.e. many particulates at a time, NSOM allows the study of this distribution one particulate at a time, including its internal structure, without special sample preparation beyond impaction onto a substrate. By operating at length scales less than the wavelength of light, NSOM has the power of optical microscopic characterization for chemical and phase information with nanoscale spatial resolution. Optical measurements can be performed simultaneously with and independently of topographic measurements which yield a three dimensional image of the particulate's physical structure. We will discuss spectroscopy, including how spectroscopic selection rules, modified due to the ability of NSOM to couple with evanescent modes, give additional information, and our initial data from ambient particulate samples.

Carbon Nanotubes and Buckyballs: Structure, Mechanics, and Air Pollutant Potential

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Ubiquitous carbon particulates contain a broad variety of particles, not always of well defined structure.¹ Recent discoveries of fullerene buckyballs and carbon nanotubes brings a new insight in peculiar properties and potential hazard of ultrafine carbon particles. We will discuss their atomic structure, unique capillary (straws) and mechanical properties. The results of simulations of nanotube behavior under different mechanical circumstances will be presented in some detail.² The applicability of continuum modeling will be demonstrated and its use for predicting nanoparticle properties. In particular their ability to damage soft tissues,³ to absorb/encapsulate and carry metals is of great importance for understanding the hazard potential. Finally, the C-C vibrational mode and their spectroscopic activity will be discussed in relation with potential high-resolution optical imaging (NSOM).⁴

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Development and Evaluation of a Condensational Growth/Virtual Impaction System for Internal Separation of Ultrafine Particles

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Atmospheric particles smaller than approximately 0.1 μm in diameter are known as ultrafine particles, or Aitken nuclei. To-date there is no epidemiological evidence linking ultrafine particles to adverse health effects of human populations, partly because health effects have always been associated with the mass concentrations of a pollutant. This does not however exclude the possibility of ultrafine particles causing adverse health effects because increased pulmonary toxicity of ultrafine particles has been demonstrated in several laboratory studies. To elucidate the toxicity of ambient ultrafine particles, inhalation toxicologists need to conduct controlled exposures to increased concentration levels of such particles by separating them from the majority of the surrounding air, while keeping them airborne.

This paper presents a method using the virtual impactor technique to separate ultrafine particles without subjecting them to a high vacuum. Our novel approach to the problem of separating and concentrating ultrafine particles using virtual impaction is to first grow the particles by condensing water vapor on them to a size that can be easily separated in a virtual impactor. After separation from the surrounding air the particles can return to their initial size by being brought back to their original thermodynamic state, using already available technologies such as diffusion dryers. The aerosol first passes over a pool of warm water (60° C) to achieve saturation. Subsequently, the air is drawn through a cooling tube (10° C) that allows the ultrafine particles to grow to micron-size. The grown particles are then drawn through a virtual impactor to be separated from the surrounding air. The effect of parameters such as sampling flow rate, ultrafine particle chemical composition, and aerosol concentration on the collection efficiency and losses of our system will be presented.

Development of a Continuous Mass Monitor by Measuring Pressure Drop Across Filters

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We have developed a continuous mass measurement method based on monitoring the pressure drop across a porous membrane (Nuclepore) filter over a period of time. Aerosol samples are first drawn through a diffusion dryer that reduces the sample relative humidity to 40% or less, and subsequently through a series of porous membrane filters. The increase in the pressure drop with mass loading has been studied for different sampling flow rates, pore size, and particle density, for particles in the size range 0.1-2.0 μm . Filters of pore size from 1 to 8 μm were tested for sampling flows varying from 0.7 to 16 LPM. The test aerosols used in the experiments included PSL latex, ammonium sulfate, sodium chloride, and indoor air particles. Aerosol mass concentrations ranged from 8.0 to 132.0 $\mu\text{g}/\text{m}^3$.

Our results showed that by appropriately choosing the face velocity and pore size of the filter, interception becomes the dominant mechanism for particle deposition. This makes the the pressure drop independent of particle size and only dependent on the mass concentration of the sampled aerosol. The pressure drop per unit time and particle concentration averages to 0.0088 (\pm 0.0005) inches $\text{H}_2\text{O}/\text{hr}/(\mu\text{g}/\text{m}^3)$ for particles in the range 0.1-2.0 μm . Our continuous mass monitoring method can detect as little as 5 $\mu\text{g}/\text{m}^3$ in about 1 hour.

We have also developed a theory that explains the mechanisms for increasing the pressure drop across Nuclepore filters with mass loading. Our sampler

was also validated in field tests by comparing its performance to collocated continuous (Tapered Element Oscillating Microbalance, TEOM) and time-integrated (Harvard Impactor, HI) samplers. Excellent agreement was found between our continuous sampler and HI for 3-hour sampling intervals, whereas HI and the continuous mass monitor were systematically measuring higher $PM_{2.5}$ concentrations than those determined with the TEOM, presumably due to volatilization losses of the latter method.

Session 10

Integrated Monitoring Study

Chair: Paul Solomon, Pacific Gas & Electric Co., San Ramon, CA

1995 Integrated Monitoring Study: Study Objectives and Design

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The California Regional PM₁₀ Air Quality Study (CRPAQS) is a multi-year, three-phase program of planning, ambient monitoring, modeling, and data analysis with the following objectives to: 1) obtain an improved understanding of the causes of high particulate matter concentrations (PM₁₀ and PM_{2.5}) in the San Joaquin Valley of California during seasons when the state and Federal PM standards are most often exceeded and 2) develop tools (i.e., air quality modeling and data analyses) that can be used by decision makers in formulating and comparing candidate emissions management practices for obtaining current and future state and Federal PM standards.

The 1995 Integrated Monitoring Study (IMS95) is part of the Phase 1 planning effort for CRPAQS, and thus, the overall objectives of IMS95 are to fill information gaps needed for planning an effective field program later this decade; to develop an improved conceptual model for pollution buildup (PM: PM₁₀, PM_{2.5}, and aerosol precursors) in the San Joaquin Valley; to develop a uniform air quality, meteorological, and emissions data base that can be used to

perform initial evaluations of aerosol and fog air quality models; and to provide early products that can be used to help with the development of the upcoming State Implementation Plan for PM₁₀. Consideration of potential new PM standards were also included in the planning and design of IMS95.

Preliminary data analysis, using existing data, indicated that the Federal PM standard was most often exceeded in the southern San Joaquin Valley during the fall and winter months, therefore, IMS95 efforts are concentrated in the southern valley during those time periods. Components of IMS95 include a two week fall study during early November (IMS95-F), a four week winter study during December and early January (IMS95-W), and a two week study of vertical fog dynamics in mid-January near Sacramento (IMS95-T). Overall nearly 100 air quality and meteorological monitoring sites were deployed during IMS95 obtaining detailed information on PM, PM precursors, fog, surface and upper air meteorology, and emissions activity data. The final data base will include supplemental data from existing sites in and near the study domain, many of which were augmented with higher frequency measurements to support IMS95. This paper will present the specific objectives of IMS95, define the study components in detail, and present rationale for sites based on the study objectives for IMS95.

1995 Integrated Monitoring Study: Fog Measurements in the Southern Valley - Preliminary Results

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One objective of the 1995 Integrated Monitoring Study is to obtain an improved understanding between the relationship of fogs and particulate matter (PM: PM₁₀, PM_{2.5}, and aerosol precursors). During the winter portion of the study (IMS95-W), surface measurements of fog were obtained during December and early January at IMS95-W Core sites located in Bakersfield, Fresno, and near the Kern Wildlife Refuge. Fog measurements, including size and full chemistry were obtained with the other gaseous, aerosol, and meteorological measurements collected simultaneously at the three sites. This paper will describe the methods and measurements employed and present preliminary results of those fog measurements.

1995 Integrated Monitoring Study: Vertical Fog Measurements in the Northern Valley - Preliminary Results

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A second objective of the 1995 Integrated Monitoring Study related to fog is to obtain an improved understanding of the vertical dynamics of fog and the relationship between fogs and particulate matter (PM: PM_{10} , $PM_{2.5}$, and aerosol precursors) above the surface. During the vertical fog or Tower study (IMS95-T), surface and aloft measurements of fog were obtained during two weeks in mid-January at a 1650 foot tower located just south of Sacramento in Walnut Grove, California. Fog measurements, including size and full chemistry were obtained with relevant gaseous, aerosol, and meteorological measurements collected simultaneously at the site. This paper will describe the methods and measurements employed and present preliminary results of those fog measurements.

1995 Integrated Monitoring Study: Spatial Variability of PM_{10} and Related Precursors During the Fall Saturation Study - Preliminary Results

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Twenty-two saturation or portable PM_{10} monitoring sites were located surrounding the core air quality monitoring site in Corcoran, California during the fall portion of the 1995 Integrated Monitoring Study (IMS95-F). Sites were placed to evaluate the representativeness of the core site and the sphere of

influence of sources within the saturation study area. PM_{10} mass and NH_3 were obtained at all sites every day for 14 days and full chemistry (ions, EC/OC, and elements by XRF) and HNO_3 were determined at ten of those sites during 9 of the 14 days. This paper will present preliminary results on the spatial variability of PM mass from this 22 station saturation monitoring network. Limited results of precursor gas and aerosol chemistry information also will be presented if available.

1995 Integrated Monitoring Study: Temporal Variability of PM_{10} and $\text{PM}_{2.5}$ Mass During the Winter Field Program - Preliminary Results

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During the winter program of the 1995 Integrated Monitoring Study (IMS95-W), PM_{10} and $\text{PM}_{2.5}$ mass and chemistry, HNO_3 , and NH_3 were collected using a three-hour sampling frequency at the four core air quality monitoring sites located at Fresno, Bakersfield, near the Kern Wildlife Refuge, and southwest of Chowchilla. These aerosol measurements were obtained simultaneously with other gaseous, fog, and meteorological measurements obtained at the core sites. The information obtained will be used to determine improved strategies for characterizing diurnal variations in PM mass and chemistry and PM precursors. This paper will present preliminary results of the diurnal nature of PM mass during wintertime conditions in the San Joaquin Valley; chemistry data will not be available until late in 1996.

1995 Integrated Monitoring Study: Surface and Upper Air Meteorological Measurements - Preliminary Results

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An extensive surface and upper air meteorological monitoring network was deployed during the winter program of the 1995 Integrated Monitoring Study (IMS95-W). Surface sites included over 100 existing sites, the addition of 5 standard meteorological sites on 10 m towers and 5 sites employing sonic anemometers at 2 m in height. Upper air measurements included existing data from the National Weather Service (NWS) rawinsonde sites in Oakland and Vandenberg Air Force Base, rawinsondes launched from Lamore Air Force Base, and a NEXRAD (NWS) near Hanford. Sites installed for the study included 4 radar profilers with RASS, two rawinsonde (4 per day) sites, a doppler acoustic sounder, and an acoustic sounder. These data will be used to characterize the three-dimensional meteorology in during the study and to provide data for model evaluation and application. This paper will present preliminary results from this network describing the meteorological conditions observed during the study and specific conditions observed leading up to and during a PM episode.

1995 Integrated Monitoring Study: Low Wind Speed Study - Preliminary Results

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The 1995 Integrated Monitoring Study (IMS95) is part of the Phase I planning effort for the California Regional Particulate Matter Air Quality Study (CRPAQS). As part of IMS95, a four-week field program was conducted (IMS95-LW) during the winter of 1995-96 to characterize mixing and diffusion under low wind speed stable conditions. An array of sonic anemometers was located in a rural field and used to collect high temporal resolution (10 hz) wind data. Tracer material (SF₆) was released at the center of the field and fifteen minute average tracer concentrations were measured at 36 locations in three rings (100m, 200m and 400m radius) surrounding the release point. The sonic

anemometer data and tracer experiment data will be analyzed to better understand mixing and dispersion under low wind speed stable conditions. This paper will describe the measurements and methods and present preliminary results of the experiment.

1995 Integrated Monitoring Study: Emissions Activity Measurements During the Fall and Winter Components - Preliminary Results

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To collect unrecoverable emissions activity data during the fall and winter programs of the 1995 Integrated Monitoring Study (IMS95-F, -W), an extensive emissions activity data collection effort was employed. This consisted of obtaining land use maps in electronic format to set up a baseline land use inventory, followed by the daily collection of activity data by specially trained operators in the field using aerial photographs, land use maps, video cameras, and data sheets. Traffic counts, using automated counters, and road silt measurements using vacuum techniques were also obtained at up to 30 sites during IMS95-F and -W programs as part of the emission data collection activities. A Microsoft Access database is being designed that will allow the emissions activity data to be easily queried through a query dialog box. This paper will describe in detail, the methods used, present preliminary results of the findings, and will evaluate the success of this unique approach to emissions data collection.

1995 Integrated Monitoring Study: Quality Assurance Methods and Results

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An integral part of the fall and winter programs of the 1995 Integrated Monitoring Study (IMS95-F, -W) was to provide extensive external and independent quality assurance (EQA) for field monitoring and laboratory analyses to ensure that data of known accuracy, precision, and validity would be obtained. An external contractor and the California Air Resources Board provided the external quality assurance effort, which included in-field system and performance audits prior to and during the measurement campaign as well as laboratory audits during the program. Essentially all measurement methods were tested, including upper air meteorological systems and special methods deployed as part of the methods evaluation. The final data base will include supplemental data from existing sites in and near the study domain, however, only data with a documented quality control/quality assurance methods and records provided by the data sponsor will be included in the final archive. This paper will describe QA methods and measurements conducted and present a summary of the results from the quality assurance effort.

Session 11

Indoor Air

Chair: Ross Highsmith, U.S. EPA, Research Triangle Park, NC

Pattern and Sources of Polynuclear Aromatic Hydrocarbons and Their Derivatives in Indoor Air

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Select polycyclic aromatic hydrocarbons (PAHs) and their derivatives were measured in several homes in Columbia (OH), by researchers at Battelle, Columbus. These homes had different indoor PAH sources such as tobacco smoke, gas/heat cooking, and electrical stoves. A combination of correlation analysis and Factor Analysis/multiple regression analysis were used to identify and apportion the different sources of PAHs. As expected, environmental tobacco smoke had the greatest impact on indoor PAH concentrations. Back round PAH were the largest contributor to total PAH in non-smokers' homes.

Real-Time Low-Level Pollution Monitoring for IAQ Applications

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Quantitative air analysis provides valuable information for indoor air quality (IAQ) investigations in airports, hospitals, museums, etc. Currently, grab sampling is the most frequently used monitoring technique. However, for certain applications real-time monitors (RTMs) are most suitable. RTMs allow solutions of a number of problems unattainable with traditional collecting devices. Using RTMs is especially beneficial when fast time response and quick analysis turnaround are required. RTMs prove indispensable in monitoring short concentration spikes, accurate measuring of low pollution levels, and applications requiring *in situ* statistical validation.

We present our results of applying RTMs to IAQ problems. We have detected ozone, NO_x, SO₂, formaldehyde, and volatile organic compounds (VOCs) with the sensitivity in the low parts-per-billion range and time response of a few seconds. Using RTMs we have determined entrainment paths of combustion engine exhaust fumes into building air handling systems, have

carried out on-site evaluation of the remaining chemical filter capacity, have performed fast and comprehensive IAQ surveys in a 3,000,000 ft² museum storage facility. We present examples when using RTMs enables better understanding of indoor air chemistry.

We also discuss future applications of RTMs and give recommendations for IAQ practitioners.

Emission Rates of Formaldehyde and Other Carbonyls from Consumer and Industrial Products Found in California Homes

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This program determined the emission rates of five carbonyl compounds from a variety of products, by testing each product in two environmental chambers maintained at realistic but different temperatures and air exchange rates. The products tested were obtained in California, and include bare wood products, coated wood products used as furniture components, cosmetics, paints, paper goods, decorative laminates, permanent press fabrics, fiberglass insulation, and industrially applied wood finishes. The five target compounds (formaldehyde, acetaldehyde, propionaldehyde, methyl ethyl ketone, and methyl isobutyl ketone) were determined by DNPH derivatization and HPLC analysis. In addition, formaldehyde was determined using a Battelle-developed continuous monitor. The monitor was used both to confirm the stabilization of chamber concentrations, for steady-state emission sources, and to follow the evolution and decay of emissions, for wet products that undergo a drying or curing phase after application. Excellent agreement was obtained between the DNPH and continuous monitor results for formaldehyde, and good reproducibility was established in duplicate tests of several products. Formaldehyde was the only target compound emitted in significant amounts from most products. The emission rates of formaldehyde ranged from less than 1 ug/m²/hour to about 1.25×10^6 ug/m²/hour. The highest emissions were found from a commercially-applied finish for wood floors. The emission rates of finished or coated wood products were a small fraction of those of the corresponding bare wood products, and emission rates of some consumer products were comparable to those of the wood products. A single washing reduced the formaldehyde emission from new permanent press fabrics by about 60 percent. The results of this study can be used to assess the importance of diverse product types as sources of indoor formaldehyde exposures.

Testing of Polyurethane Products for Emission of Toluene Diisocyanate to Indoor Air

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Polyurethane products obtained in the state of California were subjected to chamber testing to determine whether such products release isomers of toluene diisocyanate (TDI) to the indoor air in homes. The products tested included polyurethane foam carpet padding, furniture cushions, and foam mattress material; polyurethane coatings and varnishes; and caulks and sealants. Products were screened by testing groups of similar products in a 9 liter glass chamber at elevated temperature (120 °F) under nearly stagnant conditions. TDI was determined by two methods: a commercial continuous monitor that responds to total TDI, and a derivatization/HPLC method that distinguishes the 2,4- and 2,6-TDI isomers. These two methods showed good agreement in performance checks using a 2,4-TDI permeation source. In this paper the presence or absence of TDI emission from the various product types will be reported, along with quantitative emission rates where feasible.

Transfer Efficiency of Pesticides from Carpet to Saliva-Moistened Hands

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Through frequent mouthing behavior, the young child is apt to transfer pesticide residues from recently treated carpet to his/her saliva-moistened hands and mouth. An experiment was conducted to determine and compare the efficiencies of press transfer of dry residues of formulated chlorpyrifos, pyrethrins, and piperonyl butoxide from treated carpet to the palm of the volunteer's hand, which had been moistened with human saliva, an artificial saliva, or the surfactant dioctyl sulfosuccinate (DSS). Mean transfer efficiencies from plush carpet to hands moistened with human saliva, artificial saliva, and DSS were similar, with ranges of 0.7% - 1.3% for chlorpyrifos, 2.9% - 4.8% for pyrethrin I, and 1.5% - 2.8% for piperonyl butoxide. Saliva-moistened hands transferred about 100 times more dried pesticide residue from treated carpet than dry hands did. For determining moistened hand transfers, both artificial saliva and DSS appear to be suitable substitutes for human saliva.

Field-Emplaceable Air Samplers for Automated Ambient, Site, and IAQ Use

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Air samples taken on collection media for laboratory and field analysis remain a highly sensitive and cost-effective means of assessment. However, collection of samples can be difficult using non-automated samplers, particularly at remote locations. This paper describes a number of automated air samplers for sorbent-tube and filter use. The samplers are battery-powered, portable and weatherproof. They are suitable for:

Sequential sampling of 24 sorbent tubes over a period up to 1 month. This technology is suitable for long-term ambient and superfund site monitoring. A meteorological station can be integrated.

Simultaneous sampling of 4 separate media at different flows during multiple events over a one month maximum period. This technology is useful for hazard identification and location.

Very rapid sampling of dual sorbent tubes for survey use. The sampler is very small and lightweight for ease of field use.

The design of the sampling systems will be discussed, with attention paid to the sampling train and flow calibration methodology.

One case history of interest to the environmental community is the use of a variant of the 24 tube sequential samplers by the United Nations for field verification of Iraq's agreement to refrain from manufacture of chemical weapons. The units are deployed near chemical facilities and operate unattended for 1 month periods in a very severe environment. This application and the author's field trip to Iraq will be discussed.

Multi-Media Exposure Study: Rationale and Design

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Substances which may be harmful to the environment or constitute a danger

to human health require a risk assessment under the Canadian Environmental Protection Act. Since insufficient information exists for many of the substances to allow accurate assessment of their health risk, an approach for obtaining representative information on typical human exposures to selected compounds present in food, beverages, potable water and air was investigated in a multi-media pilot study. Fifty volunteers for the multi-media study were randomly selected from residents of 28 enumeration areas which were randomly selected and evenly distributed within 7 census sub-divisions (CSD) from the Greater Toronto Area. The CSD had been randomly selected from among 6009 CSD distributed across Canada in a previous study. Personal exposures to airborne target compounds over 24 h periods were measured with a passive sampler, and during the same period representative samples of food, beverages and potable water consumed by the same individuals were obtained. The target compounds were extracted from the samples, and the extracts were analyzed with GC-MS. The study design, procedures and the preliminary results will be described. The experience from this study will be used to assess the feasibility of a larger study across Canada.

Session 12

Source Sampling Methodology

*Cochairs: Merrill D. Jackson, U.S. EPA, Research Triangle Park, NC;
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Instrumentation for Continuous On-Line Monitoring of Non-Methane Organic Carbon in Air Emissions

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Non-methane organic carbon (NMOC) is a measure of total organic carbon in an air emission except that from methane. EPA Method 25 is used for quantification of NMOC in emission sources and in ambient air. This method involves laboratory analysis of collected air samples, and can not be used for real-time measurements. Permanent gases such as CO₂, CH₄ interfere in this analysis and so does moisture. In this research, a novel method for continuous, on-line monitoring of NMOC in air emissions and ambient air is presented. Detection limits were at ppb levels, and interference of permanent gases have been eliminated.

Modification of Method 25 for Low VOC Sources with High CO₂ and Moisture Levels

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The standard Method 25 has difficulties in testing for low levels of VOC in sources with high CO₂ and moisture content in the test stream. Common problems, among others, include poor method precision, high blank relative to the sample, and blockage of trap by ice during sample collection. A modification to the method was made to replace the standard trap with a small ice water impinger to drop out the moisture in the test stream, collect the polar VOCs, and control the humidity of the sample in the tank to improve recovery of non-polar VOCs during analysis. The VOCs determined as CH₄ from the water trap and the tank (SUMMA can) provide the total non-methane hydrocarbons emitted by the source. The method was evaluated in the laboratory and is being field-tested. The results will be presented.

A Test Method for the Measurement of Arylamines in Stationary Source Emissions

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Eighteen arylamine compounds are listed under Title III of the Clean Air Act Amendments of 1990 as pollutants to be regulated. Many of these compounds are suspected or known carcinogens, toxins, and irritants; and some decompose when exposed to air or light. The U.S. EPA and Research Triangle Institute, through a cooperative agreement, are developing a test method for the collection and measurement of arylamines from stationary source emissions. The proposed method of collection of arylamines is based on EPA Reference Method 5 (modified method 5 sampling train). The primary change consists of adding a strong cation exchange resin after the condenser to collect arylamines. The arylamines are analyzed using high performance liquid chromatography (HPLC) and a photodiode array (PDA) detector.

The large number of compounds, some of which are carcinogenic, made it impractical to study all eighteen arylamines. A subset of eight arylamines, representing characteristics of all the compounds, was used in the laboratory study. The analytical limit of quantitation (LOQ) ranged from less than 100 ppb for chloramben to about 15 ppm for 2,4-diaminotoluene. Considerable effort was required to identify a resin that could satisfactorily collect the arylamines and permit their removal for analysis. The LC-SCX resin, a strong cation exchange resin consisting of a sulfonic acid bonded silica, collected over 95 percent of each compound tested and retained less than 5 percent when washed with an eluant. All compounds studied were found to be stable on the LC-SCX resin.

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Method 301 Evaluation of a Technique for Collection and Measurement of Ammonia in Stationary Source Emissions

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Injection of ammonia or urea to the combustion zone of a boiler reduces the formation (and thus emissions) of oxides of nitrogen. Under certain conditions a portion of the ammonia may "slip" and may be emitted to the atmosphere. State air quality organizations have expressed interest in monitoring this and other sources of ammonia. Users of the injection technology need emissions data to assist in process optimization. In response to these needs, the EPA Office of Air Quality Planning and Standards supported laboratory development and field testing of an EPA Method 17-based procedure for quantitating ammonia at stationary sources.

This paper describes the ammonia collection and measurement method and gives results from a field test in which samples were collected at a coal-fired power plant that uses urea injection technology. Samples are taken isokinetically. Stack gases are pulled through an in-stack filter to remove particulate matter and ammonium salts, and are then bubbled through a 0.1 N sulfuric acid impinger solution to trap ammonia as ammonium ion. Ammonium in the impinger solution is assayed by ion chromatography (IC) and compared to field assay with an ammonia specific electrode. From the IC results and the sample volume, the stack gas ammonia concentration is calculated. A quadruple train assembly with dynamic spiking, as specified by EPA Method 301, was used to arrive at a precision estimate of 19.2% RSD. The bias estimate was 0.96 ppmV for a mean spiked sample value of 6.43 ppmV. The procedure met Method 301 criteria if a correction factor of 0.87 is applied.

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Development of a Manual Method for Sampling and Analysis of High Levels of Phenolic Compounds

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A method has been developed to sample and analyze high levels of phenol and cresols by collecting phenolic compounds in 2N basic impingers. Sampling and analysis for high levels (20 ppm or above) of phenol and the cresols present

special challenges to the test methodology. Because of the boiling points of these compounds, a logical choice of test methodology would be the Modified Method 5 sampling train using Draft EPA Method 3542 for preparation of the samples and gas chromatography/mass spectrometry (GC/MS) for analysis. However, at these high levels, Modified Method 5 sampling trains, even using basic impingers after the sorbent to ensure collection of the phenolic compounds, are ineffective because the standard pH-adjusted extraction techniques recover only 40-50% of the phenolic compounds from the aqueous phase condensate and the wet sorbent. A sampling method was developed to collect phenolic compounds in 2N basic impingers. Because of the high concentrations of phenolic compounds, direct analysis of the basic impinger contents by high performance liquid chromatography (HPLC) after adjustment of pH is a very straightforward analysis. For lower concentrations of phenolic compounds, the aqueous basic impinger contents can be concentrated. Laboratory studies and a field test using the criteria of EPA Method 301 have been performed. A written protocol for sampling and analysis of high levels of phenol and cresols is being prepared on the basis of the results of the field evaluation study.

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Development of an Optical Method for Sampling and Analysis of High Levels of Phenolic Compounds

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A field evaluation study designed according to the guidelines of EPA Method 301 has been performed to assess the performance of Fourier Transform Infrared Spectroscopy (FTIR) in the measurement of high source levels of phenol and the cresols. Because of the availability of data immediately in the field, optical monitoring methods such as FTIR are increasingly being applied to measurement of organic compounds in stationary sources. To allow the operation of FTIR in both spiked and unspiked modes, the system was operated extrac-tively, using a sampling manifold to allow the introduction of approximately 40 ppm of phenol and the cresols. The FTIR system was operated simultaneously with a manual method for comparison to the manual method as a reference

method. EPA Method 301 was applied to provide both an independent evaluation of the FTIR method and a comparative evaluation of FTIR to the manual method.

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Generic FTIR Sampling Method for Measuring Hazardous Air Pollutant Emissions from Industrial Point Sources

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In recent years EPA has worked to develop Fourier transform infrared (FTIR) spectroscopy for measuring hazardous air pollutants. Part of this effort was the preparation of a Protocol with the analytical procedures used to interpret infrared spectra for quantitative pollutant measurements. The FTIR Protocol has been available for public review for several years and has been successfully used in a preparation and validation of source, and compound, specific FTIR sampling methods to accompany the Protocol. These methods were necessary to address important sampling issues encountered in measuring HAPs: The chemical and physical properties of some HAPs make them difficult to handle in a conventional sampling system. An FTIR system is ideally suited for verifying the integrity of a sampling system for transporting target compounds. Recently, MRI has been preparing a Generic FTIR Sampling Method for EPA. The Generic Method contains procedures that use FTIR techniques to perform HAP measurements at a variety of sources. This paper presents an overview of the Generic Method and explains the reasoning behind its procedures.

Application of Extractive FTIR (Fourier Transform Infrared) Spectroscopy for Speciated Measurement of Uncontrolled Emissions at an Asphalt Coating Process: Sampling and Analysis Challenges at a Complex Emission Source

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Air emission measurements on uncontrolled emissions at an asphalt coating operation were performed using Extractive FTIR spectroscopy. Significant sampling and spectral analysis challenges were encountered due to the complex

effluent composition that included several HAPs and numerous volatile and semi-volatile organics. The semi-volatile species included high molecular weight aliphatic hydrocarbons that could condense in the heated sampling system and continue to be detected at low levels for an extended period. Sampling system contamination was minimized by limiting sampling time and purging between test runs. On-site QA/QC procedures included local, system, and dynamic matrix spiking calibrations with Methanol, 1,3-Butadiene, and p-Xylene. Dynamic matrix spiking was performed by injecting the three calibration compounds (with an SF₆ tracer) at the sampling probe. Acceptable calibrations and spike recoveries demonstrated the sampling system was capable of transporting these types of compounds. FTIR spectra were quantitatively analyzed for 20 compounds, with maximum possible concentrations determined for over 100 non-detected HAPs. Numerous other VOC compounds were positively or tentatively identified, but reference spectra were not available for quantitative analysis. FTIR analysis verified that most of the aliphatic hydrocarbon emissions consisted of n-Octane and n-Nonane, with only minor emissions of aliphatic HAPs (n-Hexane and 2,2,4-Trimethyl Pentane).

Method Evaluation Study: The Application of VOST to the Nonhalogenated Volatile Organic Compounds from the Clean Air Act Amendments

Merrill D. Jackson

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A laboratory study and two field studies were performed to evaluate the application of the Volatile Organic Sampling Train (VOST, EPA Method 0030) to the volatile halogenated organic compounds (approximately 35 compounds) listed in the Clean Air Act Amendments (CAAA) of 1990. Subsequently, a laboratory study was performed to assess the feasibility of the application of the VOST methodology to the volatile non-halogenated organic compounds listed in the CAAA (approximately 20 compounds). Several of the volatile organic compounds were eliminated from consideration as VOST analytes because they could not be analyzed successfully by gas chromatography/mass spectrometry (GC/MS), and others were eliminated because of poor analytical system response. The remaining CAAA volatile organic analytes (benzene, toluene, carbon disulfide, 2,2,4-trimethylpentane, and hexane) were tested in the field using the guidance of EPA Method 301 for experimental design and statistical evaluation of the data. Quadruple VOST trains were run in the field, with dynamic spiking of the volatile analytes from a certified cylinder into two of the

sampling trains. The bias and precision of the VOST sampling and analytical methodology applied to each of the volatile organic analytes were evaluated.

The information in this document has been funded wholly by the United States Environmental Protection Agency under contract 68-D4-0022 to Radian Corporation. 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.

Method Evaluation Study: The Application of SemiVOST to the Nonhalogenated Semivolatile Organic Compounds from the Clean Air Act Amendments

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A laboratory study and three field studies were performed to evaluate the application of the SemiVOST (EPA sampling Method 0010, EPA sample preparation Draft Method 3542, and EPA analytical Method 8270) to the semivolatile halogenated organic compounds (approximately 80 compounds) listed in the Clean Air Act Amendments (CAAA) of 1990. In these initial studies, PCBs, dioxins, and pesticides were excluded. Subsequently, a laboratory study was performed to assess the feasibility of the application of the SemiVOST methodology to the semivolatile nonhalogenated organic compounds listed in the CAAA (approximately 70 compounds). Several of the semivolatile organic compounds were eliminated from consideration as SemiVOST analytes because they could not be analyzed successfully by gas chromatography/mass spectrometry (GC/MS), reacted with other compounds in solution, or were insoluble in methylene chloride at the levels required to perform dynamic spiking in the field. The remaining CAAA semivolatile organic analytes were grouped as acid/neutrals and base/neutrals and evaluated in the field using the guidance of EPA Method 301 for experimental design and statistical evaluation of the data. Quadruple SemiVOST trains were run in the field, with dynamic spiking of the semivolatile analytes from a methylene chloride solution of either acid/neutrals or base/neutrals into two of the sampling trains. The bias and precision of the overall SemiVOST methodology (sampling, sample preparation, and analysis) applied to each of the semivolatile organic analytes were evaluated.

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Stack Sampling Methods for Halogens and Halogen Acids

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Sampling and quantitation of stack emissions from hazardous waste combustors and from boilers and industrial furnaces co-firing hazardous waste are required as part of the Resource Conservation and Recovery Act permitting process. Hydrochloric acid and chlorine are currently regulated, and consideration is being given to setting requirements for the similar bromine compounds. Because research information about the methods has not been published in one convenient summary, much of the technical community is unaware of its existence.

This paper will provide some of the historical and scientific background for the EPA sampling methods in use today, along with some of their strengths and limitations. The primary evaluation studies will be summarized, and publication references will be given. The SW-846 Methods Manual versions of the procedures will be compared with the versions from CFR40 part 60. Relatively new research work will be summarized, along with recent changes in the methods, and critical operating factors.

NOTICE: This is an abstract of an oral presentation to be made at the EPA/AWMA International Symposium on Measurement of Toxic and Related Pollutants at RTP, NC, May 7-10, 1996. The information in this document has been funded wholly or in part by the U.S. 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.

Development of Calibration Procedures for Toxic Metal Aerosols for Continuous Emission Monitoring Systems

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An aerosol generation system has been developed to calibrate the performance of continuous emissions monitoring systems (CEMS) for toxic metal aerosols. The U. S. Environmental Protection Agency Office of Solid Waste has

proposed the use of metals monitoring as an approach to better assess the risk of incinerator emissions. Prior to the development of metals CEMS regulations, it is necessary to determine a method to evaluate the expected performance of CEMS. To measure the performance of CEMS, a dynamic calibration approach which can be used to evaluate monitor performance must be developed and tested. This calibration approach requires stable aerosol concentrations of the 16 toxic metals on a system that has a flow rate of 20 liters per minute for the air stream containing the metals aerosol. The concentration of the metals in the aerosol must be able to vary over the range of 10 to 1000 micrograms per cubic meter, on an aerosol generating system that can operate in a stable mode for at least 30 minutes. The aerosol generation system that has been developed meets the above requirements, and has been tested in a laboratory environment.

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A Comparison of Preconcentration Procedures for GC/MS Analysis of 1990 CAAA Volatile Hazardous Air Pollutants

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The 1990 Clean Air Act Amendment specified a list of 189 Hazard Air Pollutants which require monitoring and control. Analysis of these compounds down to 0.1 ppbv by GC/MS necessitates the preconcentration of large sample volumes with subsequent water removal before injection into the GC/MS to avoid interferences during both the chromatographic separation and the mass spectral detection. Preconcentration can be accomplished cryogenically using glass bead traps, or cryogenlessly using sorbent based traps. When using cryogen, water management techniques that have successfully demonstrated utility for this application are based on either low temperature desorptions or cold trap dehydration. Water elimination using sorbent traps can be accomplished using either a dry purging technique or by using a rapid desorption water knockout trap (moisture control zone). It has been difficult to compare the relative efficiencies or effectiveness of each of these approaches as recoveries and sampling precision is a function of not only the trapping and water management technique, but of the entire instrument design and control strategy. No single instrument has been capable of performing all four of these preconcentration procedures to permit a direct comparison of their advantages and disadvantages.

An automated preconcentration system with modular traps is presented that allows direct comparison of trapping and water management procedures for both

cryogenic and cryogenless preconcentration procedures. The preconcentrator can utilize 3-stage cryogenic trapping and focusing to perform both Microscale Purge & Trap and Cold Trap Dehydration. Alternatively, trapping of the sample on a 1/8" sorbent trap followed by transfer to a 1/16" sorbent trap can accomplish both a preconcentration and sample focusing without cryogen, in which case water is removed either by dry purging or by a water knockout zone between the two traps. Precision and 5 point calibrations will be compared for many of the polar and non-polar HAP's compounds, as well as some other thermally labile VOC's. Ozone will also be added to each trapping system after loading the analytes to try to reproduce any negative bias or artifact formation that may occur during the analysis of actual air samples.

Dynamic Spiking Studies Using the DNPH Sampling Train

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The proposed aldehyde and ketone sampling method using aqueous 2,4-dinitrophenylhydrazine (DNPH) was evaluated in the laboratory and in the field. The sampling trains studied were based on the train described in SW-846 Method 0011. Nine compounds were evaluated: formaldehyde, acetaldehyde, quinone, acrolein, propionaldehyde, methyl isobutyl ketone, methyl ethyl ketone, acetophenone, and isophorone. In the laboratory, the trains were spiked both statically and dynamically. Laboratory studies indicated that formaldehyde and isophorone are efficiently recovered from the first impinger. Laboratory studies also investigated potential interferences to the method. Based on their potential to hydrolyze in acidic solution to form formaldehyde, dimethylolurea, saligenin, s-trioxane, hexamethylenetetramine, and paraformaldehyde were investigated. Dimethylolurea, hexamethylenetetramine, and paraformaldehyde all interfered with formaldehyde analysis. The sampling train containing 200 mL of reagent in the first impinger followed by two impingers containing 100 mL of reagent was then evaluated at a plywood veneer manufacturing plant. Ten runs were performed using quadruplicate sampling trains. Two of the four trains were dynamically spiked with the nine aldehydes and ketones. The test results were evaluated using the EPA Method 301 criteria for method precision ($< \pm 50\%$ relative standard deviation) and bias (correction factor of 1.00 ± 0.30). Formaldehyde, acetaldehyde, propionaldehyde, and acetophenone passed the requirements for accuracy and precision.

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Imaging Mass Spectrometry of Particulate-Associated Polynuclear Aromatic Hydrocarbons

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Time-of-flight secondary ion mass spectrometry (TOF-SIMS) was employed for the *in situ* investigation of PAHs on individual environmental particulates. TOF-SIMS is a microprobe mass spectrometry technique capable of providing surface elemental and chemical information with lateral spatial resolution $< 1 \mu\text{m}$. TOF-SIMS analysis allows for the correlation of microscopic characteristics of different particulate, filter, and sorbent substrates with absorbed organic species. Silver membrane and glass fiber filters loaded with coal flyash or silica gel were placed in a Method 0010 spiking train and exposed to vapor phase benzo[a]anthracene, benzo[g,h,i]perylene or pyrene. TOF-SIMS allowed surface chemical analysis of single particles on Ag filter media taken directly from the Method 0010 sampling train, with no additional sample preparation. Secondary ion images indicated that benzo[a]anthracene is found primarily on the filter media and not on the particulate surfaces, and is of interest with respect to the elucidation of sampling artifacts. Particulate and glass fibers were also transferred to silicon wafers for TOF-SIMS imaging. TOF-SIMS is being used to investigate the role of adsorbates in PAH quantitation by traditional solvent extraction/chromatography schemes, as well as to examine sampling artifacts, and to study photolysis or reactions of adsorbed PAH with atmospheric pollutants such as oxides of nitrogen and ozone.

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Total Organics Guidance Manual For Stationary Source Emissions

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Under contract to the EPA, a guidance manual was written to address the methods used to measure and report total organics data from stationary source emissions. Writers of air quality permit applications for waste combustion units require total organics data for their assessments. The guidance manual identifies specific techniques to determine the total organics sampled from stationary sources. To generate a value for total organics, organics data from three specific boiling point/vapor pressure classes are combined: light hydrocarbons and volatile organics (measured using Field GC and Purge and Trap GC), semivolatile organics (measured using total chromatographic organics [TCO]), and non-volatile organic compounds (measured using gravimetric analysis [GRAV]). The methods for measuring and reporting the individual parameters are discussed in detail in the guidance manual.

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Session 13

Quality Assurance

Chair: Shri Kulkarni, Research Triangle Institute, RTP, NC

NARSTO-NE Hydrocarbon Laboratory Comparison

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A laboratory comparison study was conducted as part of an external quality assessment program for the NARSTO-NE study. The objectives of the laboratory comparisons were to document significant systematic biases that may exist between laboratories, and to assess probable causes for the observed differences. Participating laboratories included Biospheric Research Corporation, State University of New York at Albany, state-operated Photochemical Assessment Monitoring Station (PAMS) networks in the NARSTO-NE study area (Connecticut, Massachusetts, Maine, Delaware, Maryland, Philadelphia Department of Public Health, Virginia, New Jersey State, and New York), USEPA Region 1 (regional reference laboratory), USEPA - AREAL (referee laboratory) and Desert Research Institute (data compilation and analysis). The laboratory comparisons consisted of a review of standard operating procedures (SOPs) used by each measurement group and performance audits using both synthetic hydrocarbon mixtures and ambient samples. This paper describes the protocol for the laboratory comparison study, summarizes the finding of the study, and examines some of the remaining technical issues facing the PAMS program and their implications.

Accuracy Considerations of Electrochemical NOX Analyzers

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Two key components contributing to measurement errors of electrochemical analyzers are discussed. These are the sample conditioning system and the electrochemical nitric oxide and nitrogen dioxide sensors. The problems

associated with various types of conditioning systems are discussed and some experimental results are presented using analyte spiking methods. Permeation drier based systems are shown to cause the smallest loss of the analyte. Two major problems of the NO and NO₂ sensors are examined. The first problem deals with the significant effect of temperature on the sensor and its associated interference rejection filter. The requirement for maintaining sensor and filter temperature below 30 deg. C is demonstrated. The second deals with the saturation and drift considerations caused by over exposure to the gas. The significance of capillary size to minimize drift for diffusion sensors is discussed. Experimental results are presented and discussed with a view to the recently published EPA CTM-022 Method.

Further Analyses of Wisconsin's Remote Vehicle Emissions Sensing (RVES) Feasibility Studies

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Previous papers have addressed quality assurance efforts with regard to collecting emissions data of known quality, data validation, and preliminary analysis of Wisconsin's Remote Vehicle Emissions Sensing (RVES) project conducted in 1993 and 1994. This paper will analyze in greater detail the field data collected over the two years of studies. This analysis includes making comparisons of mass emissions of carbon monoxide and total hydrocarbons with respect to vehicle model year and total contribution to tropospheric ozone-forming emissions in southeastern Wisconsin. A simple analysis of errors of commission and errors of omission as a function of varying RVES cut points will be reviewed. And finally, potential emissions reductions gained from the use of remote vehicle sensing will also be explored.

Quality Control Guidance for Sampling and Analysis of Air Toxics

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The inclusion of effective and comprehensive quality control procedures is critical for the performance of accurate air toxics measurements. Lack of quality control can add significant error to environmental measurements. The U.S. EPA has estimated that 95% of the total error in environmental measurements is due to sample collection and handling (85% from sample collection and 10% from subsampling in the laboratory) and that 5% occurs during laboratory analysis.

This paper provides quality control guidance for performing accurate air toxics measurements of ambient air and source emissions samples for volatile organic chemicals. The areas covered are equipment handling, field sampling and laboratory analysis. Quality control guidance for equipment handling includes checks on flow controllers, vacuum gauges, pressure gauges, manometers and canisters. Quality control guidance for field sampling includes sampling equipment checks, sample handling and field quality control. Quality control guidance for laboratory analysis includes certified standards, laboratory control samples, duplicates, blanks, internal standards, surrogate standards, instrument calibration and data evaluation. The recommended frequency and acceptance criteria for quality control procedures are discussed.

Effects of QA/QC Procedure Changes on Method 25 Analysis and 50 ppmC Method Detection Limit

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A comparison was made on samples collected (including ambient air, hydrocarbon free air, and certified master gas standards) and analyzed over a period of months. These sample sets were repeated utilizing increasing stricter QA/QC procedures. The average range of each of the sample types and the difference between them were compared for consistency. Parameters leading to potential bias such as combined small background concentrations in the recovery system, the volume sampled, cleanliness of the sampling equipment, etc. were studied.

Examination of the results suggests that by the removal or deduction of the background values the Method Detection Limit could be lowered from the current value of 50ppmC. This view is supported by the additional comparison of field sample results below using Method 25, the results demonstrate the possibility of increased applicability of this method at lower levels.

Uncertainty Analysis for Open-Path Remote Sensing of Fugitive Emissions

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Open-path remote sensing techniques such as Fourier transform infrared

(FTIR) spectrometry offer a powerful approach for determining emission rates from line, area, and volume air pollution sources. Typically, a photon beam downwind of the source intersects the pollutant plume, and a characteristic such as optical absorption is measured. The path-integrated concentration is calculated from this measurement. The emission rate can then be estimated using a tracer gas reference or by dispersion modeling.

Open-path monitoring has important advantages over conventional methods for measuring fugitive emissions. However, a different set of design and quality assurance (QA) considerations must be addressed in developing the measurement and data analysis protocols. Failure to consider the method's unique characteristics can impair the accuracy and precision of the fugitive emissions calculation. This paper will use a hypothetical area source monitored by FTIR to illustrate how the following factors can affect overall uncertainty:

- length and location of the optical path,
- release and measurement of tracer gas,
- meteorological measurements,
- selection of a dispersion model, and
- estimation of dispersion coefficients and other model parameters.

Data Quality Objectives for the Yeast Manufacturing Industry

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EPA (Environmental Protection Agency) must set a MACT (Maximum Achievable Control Technology) standard for acetaldehyde emissions from the manufacturing of yeast. Once established, the standard will apply to all existing and new yeast manufacturing facilities.

Ordinarily, the DQO (Data Quality Objectives) process would be used in the up-front planning of a data collection effort. In this case, however, the data are already in hand. Two yeast manufacturers are cooperating with EPA and have provided data on acetaldehyde emissions and yeast production. The DQO process was used to determine how these data will be used in setting the new standard.

This presentation describes the selected DQOs through Step 6 of the seven-step DQO process. Step 7, "Optimize the design," was not applicable, as data generation had already been completed by the two manufacturers. Because the manufacturers used different measurement methods, comparability became an issue. Measurement performance information will be presented and discussed.

To the extent possible, actual data will be used to illustrate how the DQOs were used to derive the proposal standard.

Overview of the ISO 14000 Environmental Management Standards

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In 1996, the International Organization for Standardization (ISO) will publish the first of a series of international standards addressing environmental management. The emerging ISO 14000 environmental management standards pose a potentially greater impact on the world community than the ISO 9000/10000 standards that preceded them. Like quality, environmental management cuts across all business sectors; however, unlike quality, environmental issues include regulatory aspects, diverse public interest groups, and an arguably broader scope of applications.

Initially, 18 standards have been proposed to encompass environmental management systems (EMS), environmental auditing (EA), environmental labeling (EL), environmental performance evaluation (EPE), and life-cycle assessment (LCA). Five standards have reached the stage of draft international standard (DIS) and two of these are the proposed EMS standards, ISO 14001 and ISO 14004.

This paper provides a general overview of the ISO 14000 standards, including their contents and their role in the overall ISO 14000 series. This paper will also briefly contrast these standards with the ISO 9000 quality management standards currently in use.

The National Ambient Air Quality Standards and Quality Assurance

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Randall G. Waite, David Musick, and Michael Papp

The U.S. Environmental Protection Agency (EPA) has established National Ambient Air Quality Standards (NAAQS) for 6 pollutants. These pollutants are carbon monoxide, lead, nitrogen dioxide, ozone, particulate matter, and sulfur dioxide. The EPA's ambient air monitoring program is carried out by State and

local air agencies and consists of four major categories of monitoring stations: State and local air monitoring stations (SLAMS); national air monitoring stations (NAMS); special purpose monitoring stations (SPMS); and photochemical assessment monitoring stations (PAMS). These networks are composed of approximately 4835 monitors across the nation. The gathering of the data from these networks is required by the Clean Air Act and 40 CFR 58. The data from these networks are used for a wide variety of purposes including: NAAQS attainment/nonattainment decisions; determining the effectiveness of air pollution control programs; evaluating the effects of air pollution levels on public health; tracking progress of State Implementation Plans (SIPS); providing dispersion modeling support; developing responsible, cost-effective control strategies; reconciling emission inventories; and developing air quality trends. Henceforth, the importance of quality data from these networks can not be overstated. The Quality Assurance/Quality Control (QA/QC) of the national ambient air monitoring program is critical. This paper discusses several major QA/QC components including: the data quality objective (DQO) process, the reference and equivalent methods program, the precision and accuracy (P&A) of the collected data, EPA's National Performance Audit Program (NPAP), systems audits, and network reviews.

A Report on the Activities of the Photochemical Assessment Monitoring Stations (Pams) Quality Assurance Work Group

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The Quality Assurance Work Group is a team of federal and state experts, formed under the auspices of the PAMS program. The purpose of the Work Group is to cooperatively explore new procedures, techniques, and strategies to ensure the appropriate level of confidence in the data collected. Four main areas of focus are:

1. **Quality Assurance and Quality Control Guidance.** The present guidance is being updated to be more specific and clear, and to include data validation recommendations, minimum data acceptance criteria, and instrument specific procedures.
2. **Data Validation and Translation Software.** Available software is being evaluated and additional software is being developed as needed to ensure that data can be processed as quickly and accurately as possible.
3. **Calibration Standards, Proficiency Studies, and Audits.** A long term strategy for providing calibration and retention time standards and for determining the appropriate frequency and type of audits and proficiency studies for PAMS sites is being developed.

4. Outreach, Training, and QA Reports. A communications and technical assistance plan is being developed.

The results of the Quality Assurance Work Group's efforts to date will be discussed.

The National Ambient Air Quality Standards and Quality Assurance

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The U.S. Environmental Protection Agency (EPA) has established National Ambient Air Quality Standards (NAAQS) for 6 pollutants. These pollutants are carbon monoxide, lead, nitrogen dioxide, ozone, particulate matter, and sulfur dioxide. The EPA's ambient air monitoring program is carried out by State and local air agencies and consists of four major categories of monitoring stations: State and local air monitoring stations (SLAMS); national air monitoring stations (NAMS); special purpose monitoring stations (SPMS); and photochemical assessment monitoring stations (PAMS). These networks are composed of approximately 4835 monitors across the nation. The gathering of the data from these networks is required by the Clean Air Act and 40 CFR 58. The data from these networks are used for a wide variety of purposes including: NAAQS attainment/nonattainment decisions; determining the effectiveness of air pollution control programs; evaluating the effects of air pollution levels on public health; tracking progress of State Implementation Plans (SIPS); providing dispersion modeling support; developing responsible, cost-effective control strategies; reconciling emission inventories; and developing air quality trends. Henceforth, the importance of quality data from these networks can not be overstated. The Quality Assurance/Quality Control (QA/QC) of the national ambient air monitoring program is critical. This paper discusses several major QA/QC components including: the data quality objective (DQO) process, the reference and equivalent methods program, the precision and accuracy (P&A) of the collected data, EPA's National Performance Audit Program (NPAP), systems audits, and network reviews.

Performance Comparison of Field-Deployable Gas Chromatographs with Canister/TO 14 Analyses

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Field-deployable and portable gas chromatographs (PGC) provide immediate data without storage of samples pending analysis, but PGC data are often trusted less than laboratory data because of the vicissitudes of field operation and because of design compromises intended to enhance the portability and sample throughput. If the capabilities of PGCs were better established, they might be used to pilot collection of data for laboratory analyses, to produce large volumes of replicate data from simultaneous samples later analyzed in the laboratory.

A comparison field study was conducted during which four commercially-available PGCs were operated downwind of a source generator. Concurrent colocated PGC and canister samples were collected. The PGC samples were analyzed immediately, and the canister samples were analyzed later by Method TO-14. Each instrument also analyzed audit standards of TO-14 target compounds kept in pressurized canisters at five different concentrations in the low ppd range. Adverse weather typical of field operating conditions complicated the study. Samples were collected, when possible, during periods of stable wind velocity and minimal precipitation. A mobile tripod-quadrupole mass spectrometer (TAGA) operating downwind of the PGCs ensured that the plume was established before each run. Agreement between PGCs and the reference method was imperfect for plume analysis data because of weather conditions. Better performance was observed when audit standards were analyzed.

Session 14

General

*Cochairs: R.K.M. Jayanty, Research Triangle Institute,
Research Triangle Park, NC;
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A Comparison of Dry Deposition Modeled from Size Distribution Data and Measured with a Knife-edge Surrogate Surface

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Numerous mass and elemental dry deposition fluxes were measured in Chicago, IL, in South Haven, MI, in Sleeping Bear Dunes, MI, and over Lake Michigan with a knife-edge surrogate surface. In general the average measured fluxes in Chicago were higher and more variable than the fluxes measured away from Chicago. In addition the most northern site (Sleeping Bear Dunes, MI) had consistently lower fluxes than the other locations. The flux of primarily anthropogenic metals (Cd, Cr, Cu, Mn, Pb, V, and Zn) was on average 1-2 orders of magnitude lower than the flux of primarily crustal elements. Atmospheric concentrations were generally highest in Chicago and lowest in the northern part of the lake. A modeling procedure that used measured atmospheric particle size distributions and modeled deposition velocities was used to calculate the dry deposition flux for comparison to the measured flux data. The average ratio of calculated/measured flux varied between 0.2 and 2. In general fluxes were slightly underestimated probably due to an underestimation of coarse particle deposition velocities. Modeling results indicate that the majority of the flux (>98 %) was due to particles >6.5 μm in size. A comparison of simultaneously measured dry depositional flux and the concentration of airborne particulate matter <10 μm in aerodynamic diameter (PM10) indicates that PM10 concentrations are not a good measurement from which to estimate dry deposition flux.

Can Selected RADM Simulations be Aggregated to Estimate Annual Concentrations of Fine Particulate Matter?

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The benefits analyses proposed for the Clean Air Act Amendments of 1990 require annual timescales. Unfortunately, most Eulerian models, like EPA's Regional Acid Deposition Model (RADM), utilized in this study, challenge the practical limits of current computer resources as well as our ability to collect the pertinent input data. As a result, application of such models to determine the long-term relationship between changing emissions patterns and ambient air concentrations is limited. To circumvent this problem, an aggregation method (initially developed for acid-deposition applications) has been modified and applied to a limited number of RADM simulations in order to provide estimates of long-term (annual) ambient air concentrations of fine particulate matter.

The aggregation method is based on the premise that at any given location, ambient air concentrations of fine particulate matter are governed by a finite number of different, though recurring meteorological regimes. If a series of concentration patterns representative of these different meteorological regimes can be identified, they can be aggregated to produce reasonable estimates of annual averages.

This paper describes how the simulation periods were selected and combined to establish long-term estimates and how representative these estimates were.

This aggregation method performed better than a random selection process.

Comparison of Risk Management Dispersion Modeling Methodologies

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Roy F. Weston, Inc.

Section 112 (r) of the Clean Air Act Amendments of 1990 requires that facilities that process, use, store, or otherwise handle substances in quantities that exceed threshold amounts develop risk management plans. The final Risk Management Programs for Chemical Accidental Release Prevention rules are due to be issued in early 1996. Facilities subject to these rules must comply within three years of rule promulgation. The basic provisions of the rules may require affected facilities to: register, conduct a hazards assessment, develop an accident prevention program, develop an emergency management program, develop a risk management plan, and provide recordkeeping. As part of the hazards analysis EPA is proposing that facilities conduct an off-site impact analysis. This paper provides the results of a comparison analysis between various dispersion models and their application to various accidental release scenarios. ALOHA, HGSYSTEMS, TSCREEN/SCREEN3, ARCHIE, and SLAB are compared for a range of release scenarios. The analysis will compare modeling results for gaseous, liquid, dense gas, neutrality buoyant, instantaneous and continuous releases. In addition, an evaluation will be made of various

release heights and meteorological conditions. The results will demonstrate which model(s) are more appropriate for the various release scenarios evaluated.

The Analysis of Ambient Air Samples for Polar Volatile Organic Compounds

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Three separate methods for analyzing polar volatile organic compounds (PVOCs) in ambient air samples are compared and the appropriateness of each method in quantifying specific PVOCs is assessed. In the first two methods, PVOCs in ambient air samples are trapped onto multiabsorbent beds, trapped water is purged from the sorbent bed with inert gas, then the samples are analyzed by either GC/FTIR/MS or high resolution gas chromatography with flame ionization detection. The third method included in the comparison consists of EPA Method TO-14, in which sample air is cryogenically trapped from polished-interior-surface stainless steel canisters and analyzed via high resolution gas chromatograph with flame ionization detection. The confounding effects of water present in samples are addressed for each of the methods in this study. Specific compounds analyzed for include methyl-t-butyl ether, methanol, ethanol, and other PVOCs of importance.

A Wind Tunnel Investigation of the Flow Structure within a Dense Gas Plume

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A wind tunnel study was performed to investigate how a dense gas plume could affect the mean flow and turbulence structure in the boundary layer. For this, a neutral atmospheric boundary layer with an aerodynamically rough surface was generated in the EPA Meteorological Wind Tunnel. The dense gas plume was simulated by releasing CO₂ through a ground-level, small circular area source. Large roughness elements were used to ascertain that the dense plume was turbulent. The initial Froude number of the dense plume was varied by changing the freestream wind speed and keeping the flow rate of the dense gas (CO₂) constant.

Special consideration was given to make accurate velocity measurements within the dense-gas plume due to the sensitivity of hot-wire and hot-film

anemometers to the CO_2 concentration. For accurate concentration measurements, fast response flame ionization detectors (FID's) were used. Flow visualization and concentration measurements indicated that buoyancy had significant effects on mean flow and turbulence structure in the dense gas plume, as well as plume dispersion.

Vertical velocity profiles were measured at the same locations as the vertical concentration profiles, both in the neutral (air) and the dense (CO_2) gas situations, so that the effects of density stratification could be discovered. In the dense plume, the mean velocity profiles were changed significantly in shape near the surface at low wind speeds. These changes were not only related to the magnitude of the CO_2 concentration, but also to the plume height; as the wind speed increased, the differences of the profiles between the dense and neutral plumes diminished. Both the longitudinal and vertical turbulent intensities were greatly reduced at low wind speeds. Shear stress and friction velocity were also considerably reduced. Appropriate scales and dimensionless parameters will be used, so that the results may be generalized. The gradient Richardson number is shown to be the most appropriate parameter for describing the changes in the mean flow and turbulence structure.

Performance Characteristics of Adsorbents Utilized in Sample Preparation Modes of Operation

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Characterization studies of both porous and non-porous adsorbents have been performed using dynamic challenge techniques. The focus of these studies was to determine the relative adsorption strengths of all commercially available adsorbents using a system which can be constructed in most analytical laboratories using commercially available equipment.

For the past several years, we have studied the adsorption characteristics of adsorbents/adsorbent tubes using both a constant challenge inlet approach and a single elution point approach. The data obtained from both of these gas-solid chromatographic (GSC) approaches provide effective insight into the performance characteristics of the adsorbents/adsorbent tubes, and assisted in normalizing the data generated over the past decade in this lab as well as other labs involved in adsorbent characterization efforts.

Also, a second on-going program in our lab is the preparation of sub-micron adsorbent particles which can be adhered to surfaces such as glass and stainless steel. The subsequent adsorption/desorption properties of the resultant surface are currently being investigated for their performance characteristics in sample preparation modes of operation.

Comparative Mutagenicity of a Standard Reference Material in the Salmonella Assay

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The purpose of this research was to determine accurate and reproducible slope values (S) in revertants/uG for a diesel extract in the Salmonella mutagenicity assay. The diesel extract was a standard reference material (SRM 1975) that was Soxhlet extracted with dichloromethane from 500 lbs of particulate material obtained from filters in operating forklifts. The SRM 1975 will be available from the NIST in 1996, along with the mutagenicity data generated here and a comprehensive analytical chemistry analysis. Mutagenicity parameters were: TA98, TA100, TA98NR, TA100NR (nitroreductase (NR) gene deficient), YG1021, YG1026 (NR gene addition), YG1024, YG1029 (acetyltransferase (AT) gene addition), and YG1041 and YG1042 (contain both NR and AT genes); 10 dose levels in the linear portion of the dose response curve; duplicate plates per dose; S9 at 1.1 mg of protein/plate; plate incorporation assay for all strains and Kado microsuspension assay for TA98, TA100, YG1021, YG1026. Results suggested: (1) mutagenic activity without S9 correlated with the presence or absence of the NR or AT genes; slope values (revertants/uG) were TA98NR(128), TA98(445), YG1021(605), YG1024(2096), YG1041(11,443); (2) the Kado microsuspension assay was 2-fold more sensitive than the plate incorporation assay (e.g., YG1021, -S9, S = 605 vs. 1317); (3) the addition of S9 significantly reduced the mutagenic activity of SRM 1975 (e.g., YG1024, plate, S = 2096 vs. 268); (4) the addition of the NR and AT genes increased the mutagenic activity of the SRM 1975 89-fold from TA98NR(S=128) to YG1041(S=11,443); (5) the TA98 series listed above was 4-20 fold more sensitive than the TA100 series in measuring the mutagenic activity of the diesel extract; (6) YG1041 was sensitive to nitroarenes at the 10 nanogram level. These data can be useful for ranking other diesel or air samples for mutagenic activity, QA of data generated in other labs, QC within a lab, and as positive control values for future air and automobile exhaust studies.

This abstract does not necessarily reflect EPA policy.

Mutagenic Activity of Raleigh Air Samples at Three Different Elevations Before, During and After Hurricane Gordon

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Diurnal ozone and VOCs were collected and measured at the Raleigh WRAL tower at three different levels: Surface, Mid (240 m), and Top (460 m) in July and August of 1993 and 1994. Measurements revealed high ozone concentrations at Mid and Top. Of the VOCs measured, only arene concentrations were significantly elevated at Mid and Top and correlated with wind direction from Raleigh. Due to arene stability, the combined presence of ozone, arenes and NO_x suggested possible arene nitration. Consequently to collect nitroarenes, samples were collected with XAD-filled canisters using high volume air samplers at the same three levels on tower days before, during, and after hurricane Gordon. Collected samples were Soxhlet extracted and analyzed with *S. typhimurium* YG 1021 and YG 1026 (+/-S9). Due to sample size limitations of collected air extracts, the microsuspension assay was used. Mutagenicity in post-Gordon stagnant air mass samples with YG 1026 was observed and the slopes (revertant/ug) were: Top (5.3) and Mid (3.3) with S9, and Top (1.7) and Mid (3.9) without S9. The Surface level, Blank, and pre- and during Gordon samples were not mutagenic. These preliminary data suggest possibility of long-term transport of mutagenic nitroarenes.

This abstract does not necessarily reflect EPA policy.

Update of EPA's Compendia of Toxic Organic and Inorganic Sampling and Analytical Methods for Ambient Air

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Air pollution has been a subject of interest and concern for many years. With the passage of the Clean Air Act of 1970, the U.S. Environmental Protection Agency (EPA) developed Federal Reference Methods (FRMs) for sampling and analysis of criteria pollutants (i.e., SO₂, NO_x, O₃, CO, and total suspended particulates) so that regulatory decisions could be based on precise and accurate data. With the passage of the Clean Air Act Amendments of 1990, the Agency now faces new challenges of regulating hazardous air pollutants (HAPs). Title III addresses the control (source/fugitive) of a list of 189 designated HAPs of which 88 percent are organic chemicals or mixtures of organic chemicals, with the remaining 21 percent occurring as particle-associated phase constituents. At this time, no uniform national program for measuring HAPs exists; rather, a number of individual, unrelated, local or State networks or special studies exist in which

a variety of monitoring and analytical techniques are used to obtain results. Consequently, the results vary widely, as does the data quality. The absence of standardized procedures raises serious concerns about the compatibility of the data collected with its ultimate use.

As awareness of this problem increased it became necessary for EPA to provide uniform, systematic, and reliable methodology to characterize HAPs in the ambient air. Through EPA's Center for Environmental Research Information (CERI) and EPA's Atmospheric Research and Exposure Assessment Laboratory (AREAL), two compendia are being developed. To address the need for monitoring methodology for organic HAPs, a revised Compendium of Methods for the Determination of Toxic Compounds in Ambient Air has been published. For inorganic HAPs, the EPA published a Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air. The objective of this paper is to discuss these two new Compendia and their applicability to characterizing HAPs in ambient air through the use of uniform, systematic, and reliable methodology. The presentation will focus on specific methodology for the following classes of HAPs.

- Atmospheric polar organic compounds;
- Atmospheric acidic and basic gases;
- Atmospheric mercury vapor and particles;
- Semi-volatile organics; and
- Sampling and analysis for atmospheric metals.

The presentation will discuss organization of the Compendia and methods format and validation. Specifically, discussions will explain how the methods are based upon performance criteria. Historically, the Agency has dictated required methodology in the Federal Register eliminating flexibility of implementation. Tenets for a performance- base approach will be discussed, including data quality objectives, calibration procedures, performance validation, and auditing process.

Estimating the Risk From Exposure to Wind-Borne Surface Soil Emissions

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Inhalation of chemicals present in wind-borne surface soil emissions can be an important route of exposure when developing a risk assessment for a site containing both erodible and nonerodible areas of exposed surface soil. The U.S. EPA-approved Industrial Source Complex Short Term 3 (ISCST3) air dispersion model was used to estimate the concentration of potential PM₁₀ surface soil emissions in air. Model input parameters and receptor locations were designed specifically for several different potential exposure scenarios being considered in

the risk assessment. A sensitivity analysis was performed to assess the effect of breathing zone height. Exposure point chemical concentrations for wind-borne surface soil emissions were calculated and evaluated for exposure to both the maximum concentration in air at a receptor point and the 95 percentile upper confidence limit for receptor points located in the area of concern for a particular exposure scenario.

Sampling & Analysis of Various Wastewater Streams at a Petrochemical Facility for Compliance with the Hazardous Organic NESHAPs (HON) Rule

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This paper will discuss the sampling & analysis methods 25D and 305 which are referenced in the HON Rule to determine compliance. The HON Rule requires the owner or operator of a Synthetic Organic Chemical Manufacturing Industry facility to determine if they will be required to control hazardous air pollutants (HAPs) from several points. Wastewater streams are considered to be a potential air emission point at these facilities, and EPA has established Methods 25D and 305 as reference methods for this determination. Samples were collected at a petrochemical facility to determine if their emissions of volatile organics would classify their wastewater streams as a Group I (requiring no control devices) or as Group II (requiring MACT). As with any new sampling and analysis procedure, errors will occur initially in understanding the applicability, in interpreting the results, and in following the methods as intended by the EPA. The methods may not have addressed all of the possible problems that could occur. The authors have been using these methods for several months, and have encountered many issues. These issues were brought to the attention of EPA for clarity and recommendations. Some of the issues that will be discussed are:

1. alternative methods;
2. sampling protocols;
3. QA/QC;
4. analytical procedures; and
5. industry concerns.

Perimeter Air Sampling Strategy for Soil Remediation at a Superfund Site

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The Arkwood Superfund Site is a former wood treating facility located in northwest Arkansas. Soil at the Site was affected by pentachlorophenol (PCP), carcinogenic polynuclear aromatic hydrocarbons (c-PNAs), and dioxin. The remedial action consisted of soil pre-treatment by dry sieving and off-Site incineration.

During the remedial action, perimeter and off-Site air monitoring were performed to ensure protection of public health and the environment. Monitoring was conducted using high volume samplers for total suspended particulates and PS-1 PUF samplers for chemical analyses. Total dust data at each downwind station was evaluated on a one to twelve work day cycle, dependent on the project schedule. The PUF sample at the station with the highest total dust reading for the cycle was submitted for PCP and c-PNA analysis. If the results exceeded the Site action levels, the sample was then analyzed for dioxin.

This sampling strategy allowed for analysis of the PUF sample reasonably suspected to contain the highest level of contaminants, thereby reducing the number of PUFs requiring analysis. Approximately 987 PUFs were collected. However, using the above sampling strategy, only 190 PUFs were analyzed. This strategy reduced the analytical costs by 80 percent.

GC/MS Analysis of Volatile Organic Compounds During Site Remediation

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Laboratory analysis of ambient air samples was performed in support of the remediation of a urban industrial facility located in the Northeast United States. Site remediation required demolition of the buildings on the site, installation of a RCRA cap and treatment of contaminated groundwater. The schedule for this work was very aggressive, with new construction over the site expected to begin 8 months after first demolition.

Since this work entailed the remediation of a site containing RCRA and TSCA regulated wastes, the methods used for the analysis of the air samples had to approach those used for the analysis of hazardous waste samples at similar sites. For this work, USEPA method TO14 was used with the QC requirements taken from the USEPA Contract Lab Program Volatile Organics Analysis methods with slight modifications.

Results for all of the QC obtained during the analysis of the air samples associated with this project shall be presented, with special emphasis placed on the use of surrogates added to the SUMMA Passivated canisters prior to sampling.

Evaluation of Sludge Characteristics and Source Emissions from Municipal Sewage Sludge Incinerators

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The United States Environmental Protection Agency (USEPA) has promulgated regulations affecting the disposal of municipal sewage sludge under Title 40 of Code of Federal Regulations (CFR) Part 503. The paper will address emissions requirements for sewage sludge incineration under 40 CFR Part 503 Subpart E. The paper will focus on factors which influence sewage sludge characteristics, sludge metals feed rates, and the corresponding metals emission rates.

Test programs were conducted at three municipal sewage sludge incinerators to measure metals emissions rates. Concurrent to source testing, metals content in the influent sludge feed to the incinerator were also measured. Metals emissions were determined using USEPA Method 29, and sludge metals determination was based on USEPA Method SW846. The results from these programs will be analyzed to identify the factors that may influence the metals emission rates. Particularly, emission rates of toxic metals such as mercury, cadmium, and arsenic will be evaluated in detail. Metals removal efficiencies by the installed air pollution control equipment will be quantified. Additionally, unique sampling and analytical issues encountered in these test programs will also be addressed.

Session 15

Human Exposure

*Cochairs: M. Rodon-Naveira, U.S. EPA, Research Triangle Park, NC; and
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Using Environmental Exposure Data to Set Environmental Health Priorities/Interventions in a Community Setting.

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An expanded role for environmental/human exposure data is emerging relative to the identification and prioritization of potential health risks in communities and defining the appropriate research and intervention strategies. This exposure-to-disease approach can be integrated with traditional environmental monitoring and public health models to produce a more appropriate environmental health paradigm. Such a model will be described in this presentation as well as the additional research and data bases needed to strengthen its application.

This is an abstract of a proposed presentation and does not necessarily reflect EPA policy.

Evaluation of Field Methods for Estimating Exposure of Children in Low-Income Families to Polycyclic Aromatic Hydrocarbons

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Children in low-income families are thought to have higher exposures to polycyclic aromatic hydrocarbons (PAH) and related compounds than children in higher-income families. These higher exposures could result from the location of their homes, nearer to industrial sites and traffic; from poorer diet; from environmental tobacco smoke; or other causes. This study was designed to

evaluate methods and estimate total exposures of low-income children to PAH through various pathways. Nonsmoking participants with preschool children, incomes at or below the official US poverty level, and space heating in their homes were recruited. The PAH concentrations were measured in the household indoor and outdoor air, house dust, yard soil, and diet, and urinary metabolites of PAH were measured for both an adult and a preschool child living in the home. A preliminary study in two homes and an additional study of eight homes, half urban and half rural, during the heating season have been completed. The problems and successes encountered in the recruitment process and the results of the heating season measurements will be discussed.

This abstract 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.

Measuring and Modeling Indoor-Outdoor Pollutants in a Residence Using Real-Time Methods

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State-of-the-art, real-time monitors were used to measure carbon monoxide (CO), fine particles, particle-bound polycyclic aromatic hydrocarbons (PAH), and ozone (O₃) indoors and outdoors at 5-minute intervals in a California residence over a period of 1-1/2 years. The 18-month study period allowed seasonal changes to be examined in this Residential Exposure Project, and the high time resolution of the monitors allowed individual outdoor sources (motor vehicle, wood smoke) to be identified. The house — a 4 bedroom, occupied home — was free of indoor sources during most of the monitoring period, allowing a mathematical indoor-outdoor model to be developed and evaluated. The mathematical model was used to predict the indoor concentration time series from the outdoor time series, and the model included parameters for the ventilatory air exchange rate, the decay rate due to deposition on indoor surfaces and removal processes. By examining an outdoor ambient episode for CO and PAH_{2,3,6}, it was possible to determine all the decay rate parameters for the model. This analysis showed that the penetration factor included in prior indoor air quality models actually was unity and could be eliminated from the equations. The predicted indoor concentration time series for all four pollutants was calculated from the model using the observed outdoor time series as the input.

and the resulting predictions were compared with the observed indoor time series. The effect of varying air exchange rates on the model predictions was examined. Regression of the predicted indoor time series on the observed indoor time series shows that the model can accurately determine indoor concentrations of the pollutants, given accurate values of the individual parameters.

Demonstration of Real-Time Measurements of PAH and CO to Estimate In-Vehicle Exposure and Identify Sources

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Significant inhalation exposures to polycyclic aromatic hydrocarbons (PAH) and carbon monoxide (CO) may occur in motor vehicles due to vehicular emissions of these contaminants, the proximity of the occupant to the source, and the amount of time spent commuting. Portable measurement instrumentation has recently become available so that real-time particle-bound PAH can be measured simultaneous with real-time CO. These new instruments were coupled and used in a commuting study to evaluate the concentrations and variability of CO and PAH inside motor vehicles in traffic. Measurements were made on 11 trips in each of two cars (22 total) over prescribed routes in two locations (North Carolina and California). This paper describes the measurement methodology and demonstrates the utility of the measurements in assessing short-term transient exposures and in distinguishing exposures from diesel or gasoline fueled vehicles.

This abstract 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.

Cooking as a Source of Fine Particles: Experiments in a Townhouse

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Experiments were carried out in an occupied townhouse to determine a) the effects of cooking on fine ($PM_{2.5}$) particle concentrations indoors; and b) the decay rate on interior surfaces of aerosols created by heating cooking oils. It was found that cooking with oil could elevate fine particles by amounts ranging between 10 and 100 g/m^3 , and a few seconds with the oil hot enough to emit visible smoke were sufficient to elevate levels to between 150 and 1000 g/m^3 .

Seven experiments to determine the decay rate for k of $PM_{2.5}$ particles on interior surfaces resulted in a value for k of $0.33 \pm 0.08 \text{ h}^{-1}$. This value was in agreement with the value for $PM_{2.5}$ particles of $0.39 \pm 0.18 \text{ h}^{-1}$ estimated from statistical analyses of 178 Riverside, CA, homes.

Biases in Personal Aerosol Air Exposure Sampling

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Recent examination of various aspects of personal aerosol sampling suggests that phenomena such as the "personal cloud" may significantly bias the relationship between a monitor worn on the body and one in a fixed location in common microenvironments. Particles greater than about $1 \mu\text{m}$ were shown in laboratory and residential settings to be resuspended from certain indoor surfaces while walking, increasing significantly the average room concentrations. Levels of $PM_{2.5}$ increased only slightly in residential settings, while PM_{10} levels increased substantially by over $50 \mu\text{g}/\text{m}^3$.

The presence or absence of a "bluff body" simulating the physique of a person during fixed location sampling can also influence the aerosol mass concentration. Controlled tests using an Aerodynamic Particle Sizer were conducted to determine the sampled size distributions penetrating personal sampler inlets. These preliminary tests suggest that fixed-location aerosol sampling for PM_{10} , without a form simulating the human torso (behind the inlet), significantly overestimates the exposure to 2.5 to $10 \mu\text{m}$ particles that would be made with the same inlet worn on the body. Based on limited data, the levels of computed mass concentration average 15 to 20% greater without a bluff body behind the inlet for both $PM_{2.5}$ and PM_{10} size fractions.

Strategies for the Development and Application of Screening Techniques for Human Exposure and Environmental Assessment Surveys

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Exposure assessment studies are frequently hampered by the lack of suitable low-cost analytical methodologies. The EPA NERL CRD-LV is addressing this issue by developing and applying technologies for implementation into monitoring studies. The CRD-LV immunochemistry program has investigated the use of

immunoassays for the detection of pesticides in foods and dislodgeable residues. Supercritical fluid extraction has been coupled successfully with immunoassays to analyze heterogeneous food matrices. Methods for several widely used pesticides (e.g. atrazine, carbaryl, metolachlor, etc.) Are being refined for use in exposure assessment surveys. An immunoassay for chlorpyrifos is being adapted to a wide range of food crops (e.g. peach, cucumber, nectarine) to rapidly measure dislodgeable residues in the field to determine safe re-entry. Due to their widespread distribution and acute toxicity characteristics, phenolic compounds show a potential for human and ecosystem exposure. Because these compounds are difficult to measure using standard methods, even under laboratory conditions, methods for screening these compounds in the field could be of considerable value. Results will be presented describing an enzyme-electrode for detection of phenolics. These results will also include the characterization of this biosensor with respect to 20 environmentally significant phenolics (i.e. compounds listed as ATSDR Priority Hazardous Substances.) The CRD-LV is also investigating the teaming of conductive electroactive polymers with antibodies to develop a reusable immunosensor. These electroimmunochemical methods show promise for the continuous monitoring of waste streams and ground water. Methods for pesticides and the polychlorinated biphenyls will be discussed.

The Exposure Potential Matrix: A Dietary Model Using Extant Databases to Evaluate Exposure to Chemical Residues

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Dietary modeling is used in USEPA/NERL's monitoring programs to identify the relative importance of diet to other pathways of exposure and to indicate when more comprehensive assessments or measurements are warranted. Dietary exposure modeling will indicate the potential for high exposure of the US and regional populations, and for certain sub-populations caused by high consumption of a particular food, or a highly contaminated food, or unique dietary characteristics, such as regional and ethnic influences.

In many cases the information needed to characterize the dietary intake of an environmental contaminant may be obtained from existing databases on food and drinking water consumption and contaminant residue levels. An inventory of such dietary data was followed by the creation of a personal computer-based dietary exposure model and database system, termed the Exposure Potential Matrix (EPM), that correlates food consumption and contaminant residue information in a format for exposure modeling. Currently, consumption information is based on USDA National Food Consumption Surveys (NFCS) conducted from 1977-92. The contaminant residue database available to EPM includes

government-sponsored monitoring programs, such as the FDA Total Diet Study (TDS), the Pesticide Residue Information System (PRIS) and the California Pesticide Monitoring Program. Residue information from the national databases are extracted, limits of detection are determined from methods codes or follow-up with laboratory analysts, and custom residue databases are created for the EPM. Consumption is based on 10 food groups containing approximately 800 exposure core food types, established from over 6500 common food items, that provide a logical format for linking the contaminant residue information to the consumption databases through recipes developed for exposure analysis.

Though not intended for risk analysis, the EPM will be useful for human exposure measurement programs to identify highly consumed and highly contaminated food items that potentially account for the majority of dietary exposure to a specific contaminant. Ongoing efforts are directed at testing the EPM and expanding it through the inclusion of additional, relevant and more recent consumption and residue databases. A current version of the EPM is available for demonstration and participant review.

Quantitative Analysis of Road and Carpet Dust on Shoes

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The goal of this preliminary study was to test the hypothesis that there is preferential track-in of small particles by measuring the quantity and size distribution of dust on a smooth vibram shoe sole after a walk over 1) standard Arizona road dust, 2) a carpet embedded with such dust, 3) a clean carpet following a dust walk, and 4) a suburban road with unpaved shoulders. The concentrations of lead in the road and carpet dust were also compared.

The dust was placed in a box and walked on with a shoe to determine the number of steps on the dust required to achieve a maximum shoe dust load. A similar experiment was done to determine the minimum number of steps by a dusty shoe on a carpet required to produce a minimum shoe dust load. Samples were collected from shoes after walking on:

1. dust;
2. a carpet embedded with dust;
3. a clean carpet after walking on dust;
4. and a suburban road.

3M transparent Magic tape was used to lift the particles off the shoe sole

after each test for automated image analysis. Each experiment was repeated six times. Finally, the concentration of lead in the dust and in a carpet was compared after extensive tracking from the dust to a clean carpet. The dust in the carpet was sampled with the High Volume Small Surface Sampler (HVS3).

Conducting Child Behavior Studies to Identify and Characterize Pathway and Route of Exposure Through Direct Observation and Videotaping

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The Office of Pesticide Programs (OPP) and the Office of Pollution Prevention and Toxics (OPPT) have recognized the study of human activity patterns in certain environments as an important issue in the regulatory oversight of chemicals, particularly, pesticides and other consumer products, in residential environments. In response, the National Exposure Research Laboratory (NERL) in Las Vegas initiated a program to identify human activities of sensitive populations, particularly children, that caused them to contact and transfer surface residues in residential environments. Infants and children were chosen as the sensitive population focus group because, as identified by the Select Committee on Children, Youth and Families, (Environmental Toxins and Children: Exploring the Risks, Part I, 1991), children have greater skin surface area to body weight, they perform daily activities in close proximity to contaminated surfaces, and they are undergoing rapid development of tissues, organs, and organ systems. Moreover, little is known about the activities of children that lead to random or incidental exposure to chemicals used in the home.

As a first step, NERL Las Vegas needed to draw together behavioral, technical, and exposure assessment information into a focused protocol for studying non-occupational, or more precisely, incidental exposure of children in residential environments. To accomplish this first step, a program was designed to explore the pediatric and behavioral science literature for activities such as "hand-to-mouth" activity that could be used to explain exposures such as geophagia and pica, the eating of soil and extraneous matter. The activities of children were compiled into various demographic groups by age, sex, ethnicity and parental guidance. Statistical prior distributions of activities were established based on demographic characteristics. In the next step, the prior distributions

were then tested against data obtained from a field study as a prototypical day care center where the behavior of children were directly observed by experts and by videotaping. What emerged from these studies was a data base of distributions for certain patterns of behavior that when examined against the biomechanics of contact and transfer of surface residues through video analysis could be used to predict exposure to children in residential environments without their involvement in human subject testing.

The National Human Activity Pattern Survey (NHAPS) Applications for Exposure Assessment

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The National Human Activity Pattern Survey (NHAPS), a two-year probability-based telephone interview survey of 9,386 individuals, was conducted to fill a need for updated activity information on a nationwide scale. Recent exposure monitoring studies have shown that human activities play a critical role in explaining variation in human exposure because they impact the frequency, duration, and intensity of exposure to pollutants. Activity pattern data bases with adequate potential pollutant exposure information have been available only for a few cities (e. g., Cincinnati, Denver, Washington, DC) or a state (California), and only for limited months of the year. The NHAPS was performed for the USEPA from October, 1992 through September, 1994, by the Survey Research Center at the University of Maryland, College Park, to ascertain the time, location, and other characteristics of activities which are most relevant to estimating pollutant exposure. Respondents provided recall of sequential events from the preceding 24-hour day as well as answers to follow-up questions for activity and location of exposure-related occurrences. Time-activity data can be effectively used in several types of statistical analyses, including descriptive, relational, temporal, and exposure modeling. Also, the analyses can be defined by various levels of characteristics. For example, the micro-environmental components can be summarized by temporal factors (time of day, day of week, season), by spatial items (region, state), by demographic elements (age, gender, ethnicity, years of education), and by frequency and duration of occurrence. The NHAPS survey design, data base configuration, and statistical analyses results will be presented and discussed. Examples of how the NHAPS time-activity data base can be used to refine current human exposure models will be described.

Application of Human Activity and Microenvironmental Concentration Data Models in THERdbASE to Exposure Assessment

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Abstract not available.

Applying Results from Ecological and Human Exposure Monitoring Studies for Reducing Risks and Prioritizing Future Environmental Health Research

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The need for total environmental exposure information in assessing risks and developing risk management strategies is only a recent phenomenon. Despite its importance, assessment of total human and ecosystem exposure has been relatively neglected as an area of research. This may be a result of media-specific legislation, such as the Clean Air Act, Clean Water Act, and Safe Drinking Water Act. Another obvious reason is due to the fact that the U.S. Environmental Protection Agency (EPA) has been organized along media lines, for example, Office of Water and Office of Air and Radiation. As a result, the total environmental health research field which incorporates exposure information from all the media relative to a human and/or ecological receptor is relatively new with a very limited data base from which to draw upon when developing risk management strategies and developing risk-based research priorities.

The objectives of this presentation are to illustrate by way of recent total exposure monitoring studies that (1) monitoring results will reduce the uncertainties associated in the risk assessment process; (2) total exposure information can be used to develop cost-effective risk reduction strategies; and (3) results from these studies provide useful information to prioritize research projects and to develop efficient exposure study designs. Advantages and disadvantages associated with use of common and newly developed environmental and biological indicators in relationship to the above mentioned objectives will also be discussed.

Evaluating Food Contamination Scenarios for Dietary Exposure Studies

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Of the three major exposure pathways (inhalation, adsorption, ingestion), ingestion may account for significant exposures to many hazardous environmental contaminants. Dietary exposure research is now considered an integral part of the U.S. Environmental Protection Agency's (EPA) Human Exposure Research Program. For dietary exposure to occur, foods contaminated with hazardous chemicals must be available and consumed. Major sources of contamination include commercial and noncommercial (i.e., home gardening) food supplies. Alternatively, uncontaminated food supplies may be contaminated by incidental contact in a polluted microenvironment. Over the years, regulation and monitoring of commercial food supplies has been the responsibility of the Food and Drug Administration (FDA). EPA's research, on the other hand, should provide information on important pollutant exposures through unregulated sources of contaminated food.

The purpose of this research is to test the hypothesis that "food stored, prepared, or eaten in a contaminated microenvironment" will serve as a vehicle of dietary exposure to chemicals in that microenvironment. Throughout this project, testing has been conducted to determine the extent to which VOCs, pesticides, and lead will partition from air, water, and exposed surfaces into various foods using controlled sorption studies, to generate partition parameters that can be used to predict food contamination with these pollutants under actual environmental conditions, to measure pollutant uptake by food during cooking with contaminated water, and to measure actual contamination of lead, pesticides, and VOCs through a series of field monitoring tests in contaminated microenvironments including homes and gas stations.

Results have shown substantial contamination of foods for all pollutants and all contamination scenarios (air, surfaces, and water). As an example, foods boiled in lead-contaminated water will absorb more than 80% of the lead from the water. Similarly, foods serve as very strong sinks for VOCs in air; equilibrium partition experiments have shown rapid and quantitative adsorption of VOCs onto foods. Details will be provided on the experimental approach and the resulting data. Implications of these results for designing dietary exposure studies will also be discussed.

Although this research was conducted as part of EPA Cooperative Agreement CR 822070-01-D, it has not been subjected to the required peer and administrative review and does not necessarily reflect the views of the Agency, and no official endorsement should be inferred.

Measurement of Street-Level Air Pollutants in Bombay City

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Abstract not available.