

THE CARBON MONOXIDE-ELEMENTAL CARBON LINK:
A METHODOLOGY FOR DIAGNOSING AND MONITORING SOOT IN URBAN AREAS

Darrel Baumgardner¹, Graciela Raga and Oscar Peralta
Centro de Ciencias de Atmósfera
Universidad Nacional Autónoma de México
Mexico City, Mexico

BACKGROUND

Carbon monoxide (CO) and elemental carbon (soot) are produced in large quantities by incomplete combustion in urban areas. The effects of soot on health (*Dockery et al.*, 1992, 1993), photochemical processes (*Raga and Raga*, 1999) and on structural damage (*Mansfield et al.*, 1991; *Pio et al.*, 1998) has raised the scientific and public consciousness of the need to better understand and monitor soot formation, evolution, and transport, as well as its catalytic potential for surface heterogeneous reactions. The measurement and monitoring of CO is common in the large urban areas of first world countries and becoming more frequent in the cities of developing countries. The measurement of soot mass is more problematic because of its particulate nature and difficulty in quantification; however, because of its ubiquitous nature and potential for environmental damage at so many different levels, there is a serious need to assess its magnitude, both spatially and temporally. Recent measurements in Mexico City show a high correlation between CO and the light absorption coefficient, σ_a , and optical property of aerosols that is linearly related to the mass mixing ratio of soot (*Fuller et al.*, 1999). As a result, there is a possibility that CO can be used as a surrogate for soot concentrations if the physical basis for the link between these two atmospheric components is well understood.

There is a obvious link between CO and soot since both are produced in abundance during inefficient combustion processes. The formation of soot depends on the carbon/oxygen ratio in the hydrogen-air mixture during combustion. The combustion stoichiometry is (*Seinfeld and Pandis*, 1998)



where C_s is the soot formed and the ratio of carbon to oxygen is $m/2a$. The C/O ratio is critical for determining the amount of soot formed, i.e. if there is sufficient oxygen to tie up all available carbon as CO, then no soot will form. With less and less oxygen, more soot is formed. Thus, one would expect the relationship between CO and σ_a to be related to altitude, fuel composition, and combustion efficiency.

In the following sections, the measurement techniques and sampling site will be discussed, followed by an analysis of five, continuously high pollution days that represent typical conditions in a urban area. The presentation is closed with some preliminary conclusions and recommendations for additional studies.

MEASUREMENT AND ANALYSIS METHODOLOGY

The experimental site was located within the Mexico City Ajusco Ecological Reserve (19° 15' N, 99° 11' W), in the southwest corner of the Mexico City basin, at an elevation 440 m above the average city level of 2240m. This site provided measurements in the residue of the city's mixed layer at night and early morning, and in the polluted mixed layer that enveloped the site during the day. The field campaign extended from 4 to 18 November 1997, a period that is normally near the end of this region's rainy season.

Continuous measurements at a sampling rate of 1 Hz were made of carbon monoxide (CO), sulfur dioxide (SO₂), nitrogen oxides (NO, NO_x) and ozone (O₃). The total scatter and hemispheric back scatter coefficient of aerosols were measured at three wavelengths (450, 550, 700 nm) with a nephelometer and the absorption coefficient, σ_a , with a particle soot absorption photometer (PSAP, Radiance Research Corp.), after the particles were first passed through a 1 μ m cut-size impactor and heated to insure a relative humidity less than 40%. The PSAP measurements were corrected for light scattering and other effects that bias the absorption measurements using the suggested factors of *Bond et al.* (1999). The optical coefficients were averaged at one minute intervals, and taken 24 hours a day. Visible and ultraviolet solar radiation

¹ also affiliate scientist, National Center for Atmospheric Research, Boulder, CO

were measured with hemispheric radiometers. Meteorological measurements (wind speed and direction, temperature and relative humidity) were also recorded. The equipment was installed in a building within the Reserve, with all gas and aerosol samples taken from air coming through a chimney that extended above the building by approximately two meters (a total of approximately 8m above the ground) and ventilated with a flowrate of approximately $90 \text{ l} \cdot \text{m}^{-1}$. The meteorological measurements were made at the same elevation as the top of the stack, about three meters to the north. All the measurements were processed into six minute averages that corresponded to the accumulation interval of the DMA.

The remainder of this paper focuses on the measurements made of CO , σ_a , and wind.

RESULTS AND DISCUSSION

Five days during the research period were selected for the evaluation of the $\text{CO} - \sigma_a$ relationship, November 14-18, 1997. These days were selected since they are days with high ozone levels representative of the typical high pollution days in Mexico City. Figure 1 illustrates the daily trends in CO , O_3 , and σ_a over this five day period.

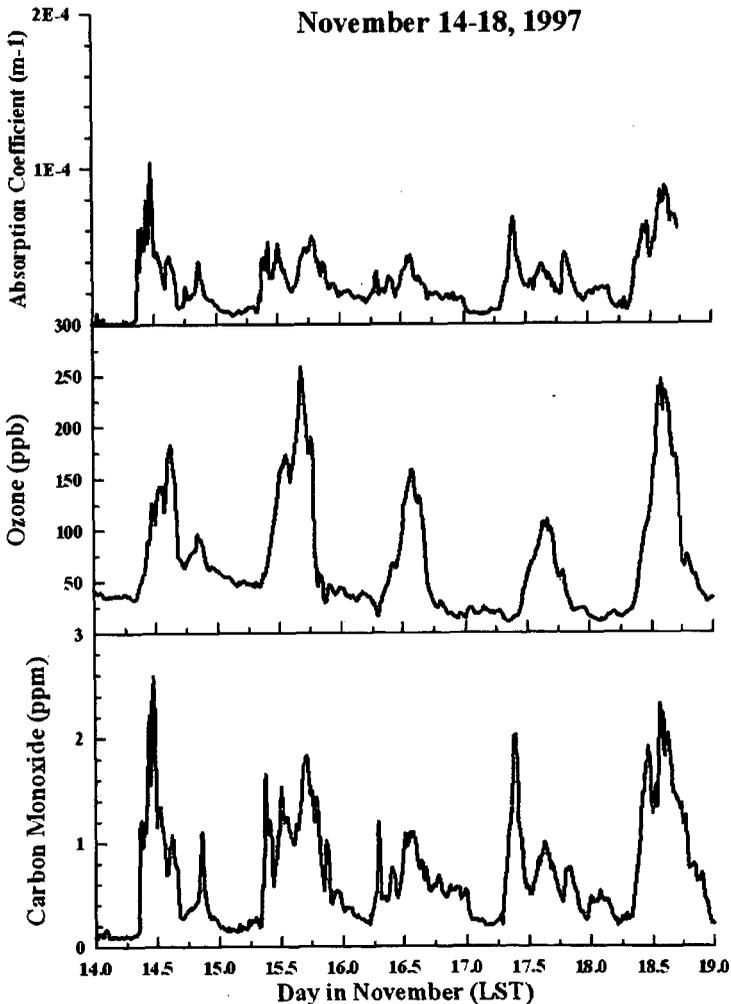


Figure 1

The initial rapid increase in CO occurs as the morning airflow shifts to a southwesterly direction and emissions from early morning traffic are transported up the hillside to the research site. As the sun rises and heats the Mexico City basin, the atmospheric mixed layer develops and grows to an altitude higher than the measurement site. Ozone increases with increasing actinic fluxes during the day. The relationship between CO and σ_a is clearly seen in Fig. 2 as the trends for one of the days, November 14, are displayed for the time period between 6:00 and 18:00 LST.

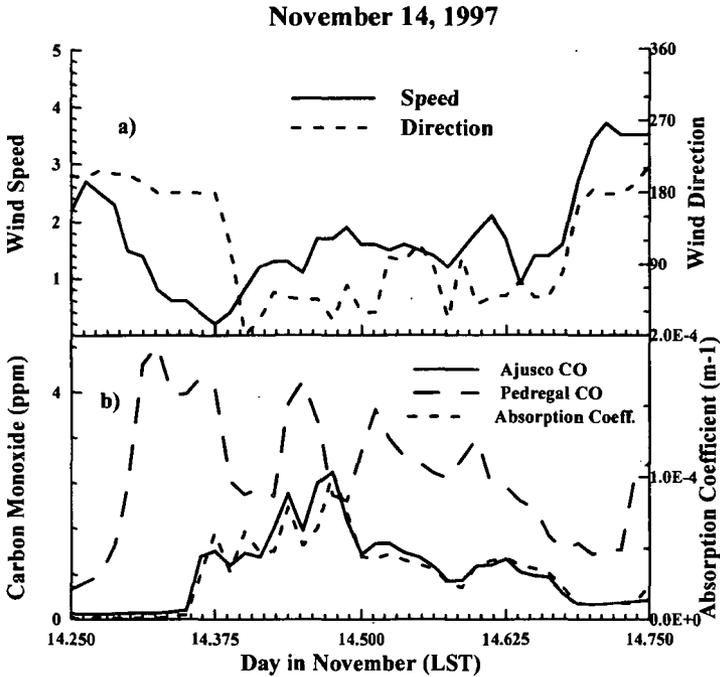


Figure 2

Figure 2b clearly shows that the σ_a changes with CO at the research site. Also presented in this figure is the CO measured upwind, in the city basin at one of the city's pollution monitoring sites (Pedregal). This particular research site is approximately two kilometers to the north of the Ajusco. When the winds are southerly at average speeds of 2 ms^{-1} (Fig. 2a), the CO measured at the Ajusco site represents the city level CO that has aged approximately one and a half hours. The CO normally decreased by about 50% from the city to the research site. This decrease occurred mostly as a result of dilution.

Figures 3 and 4 are scatter diagrams of σ_a Vs CO for all five days (Fig. 3) and four the 14, 16, and 17 of November only. The linear regression of σ_a as a function of CO, and Pearson correlation coefficient were computed and are shown on the two figures. These figures indicate a very good linear correspondence between σ_a and CO, reflected in statistically significant correlation coefficients, i.e. an indication that a first order polynomial fits the data well with high confidence levels. There is a certain degree of scatter, however, a group of points that appears to have a similar slope as the best fit line, but with an offset that could either be a decrease in σ_a or increase in CO. These data originate primarily from November 15 and 18, as seen in Fig. 4, where these days have been removed from the analysis. The slope and offset of the best-fit line, excluding these two days, is not significantly different and the correlation coefficient increases only slightly.

Further analysis of the relationship between σ_a and CO, with respect to meteorological conditions and other anthropogenic emissions, e.g. O_3 and NO_y , indicate that the linear regression coefficients of σ_a Vs CO remain remarkably constant regardless of local meteorology or other emission indicators.

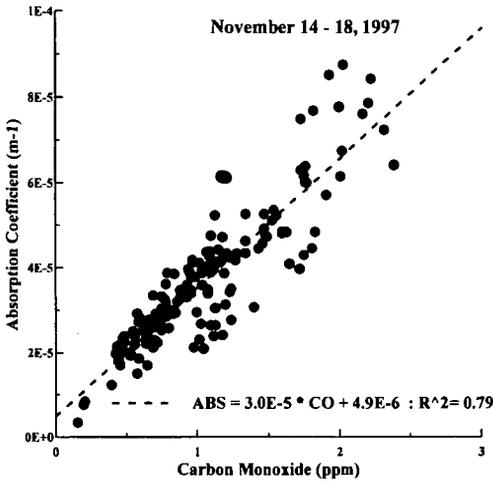


Figure 3

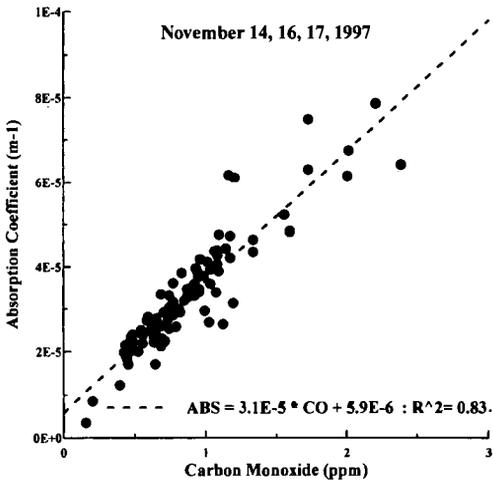


Figure 4

The positive offset, indicated by the non-zero intercept of the best-fit line, suggests that there is possibly some type of hysteresis that occurs on a daily basis, i.e. that there is a residual of soot aerosols that remain aloft when the mixed layer decays in the afternoon. When the five days were analyzed on an individual basis, although the slopes of the best-fit lines remained approximately 3×10^{-5} , the offsets ranged from $1 - 12 \times 10^{-6}$. This might be related to the previous days soot levels and maximum height of the mixed layer; however, additional evaluation of the measurements are needed before this can be better ascertained.

SUMMARY

As the amount of soot and CO produced by combustion is proportional to the type of fuel that is used and the amount of available oxygen, it is likely that the soot-CO relationship can vary from city to city. In addition, the current measurements were made several kilometers distant and 1-2 hours of aging downwind of the primary sources. Since the mixing and dilution processes are different for gases and aerosols, the CO- σ_a relationship may possibly depend upon the distance from emission sources, as well.

The ability to estimate soot from CO measurements is highly promising, however, because of the ease of measuring CO compared to soot, the abundance of past CO measurements that could be analyzed with this relationship, and the potential for better monitoring of soot in the future. Evaluation of this relationship continues at UNAM with a current focus on measuring CO and σ_a closer to emission sources in the city. The evaluation will concentrate on further refining the CO Vs σ_a relationship and understanding how other factors potentially affect this relationship.

The absorption coefficient is a useful parameter for assessing decreases in optical depth and the subsequent effect on radiative fluxes and impacts on photochemistry and climate change. The soot mass, however, is very important when evaluating the impact on health and heterogeneous processes. Hence, filter samples of aerosols are being analyzed to measure the soot mixing ratio. These will be used to estimate the specific absorption of Mexico City soot in order to convert absorption measurements to mixing ratios.

ACKNOWLEDGEMENTS

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Examination of Hydroxyl Polycyclic Aromatic Hydrocarbon Isomers Using Time of Flight Mass Spectrometry

Qin Chen*, Juan Suro, Peter B. Kelly

Department of Chemistry, University of California, Davis, Davis ,CA95616, USA

Key Words

Time of flight mass spectrometry
Polycyclic aromatic hydrocarbons
Photochemistry

Introduction

Determination of toxicity and health effects associated with particulate matter requires chemical speciation of the aerosol. Particulate matter formed by combustion processes contain a wide variety of polycyclic aromatic hydrocarbons (PAH) and their derivatives. PAH derivatives, such as nitro-PAHs, have significantly larger biological activity than unsubstituted PAHs. Exposure of the particulate matter to NO_x , SO_x , and photochemical atmospheric processes can produce substituted PAHs. Aromatic sulfonates have been studied as a contaminant in association with municipal waste water.[1] However, little is known about the possible effects of these hydrophilic aromatic sulfonates on the environment or about their degradation in the atmosphere.

Analytical tools for the qualitative and quantitative determination of highly water-soluble aromatic anions at the trace levels in aerosols have not been available. Currently, liquid chromatography is the most commonly used technique for detecting highly polar aromatics. However, liquid chromatographic methods require a large sample size and multiple runs [2][3].

Laser Desorption Ionization Time-of-Flight Mass Spectrometry (LDIMS) has proven to be an effective method for detection of trace levels of polycyclic aromatic hydrocarbons (PAHs) and PAH derivatives [4][5] in airborne particulate matter. This paper discusses the use of LDIMS to examine two naphthalene sulfonate isomers (1-naphthol-4-sulfonic acid and 1-naphthol-3-sulfonic acid) and nitro-naphthanol isomers to study the structural information as well as possible photochemical reactions from the mass spectra.

Experimental

Two isomers: sodium salt of 1-naphthol-4-sulfonic acid (1,4-SNS) and sodium salt of 1-naphthol-3-sulfonic acid (1,3-SNS) were chosen for study. Both were purchased from TCI America (Portland, Oregon) and used without further purification. Each compound (10 mg) was dissolved in 1 ml methanol, and was mixed with 9 ml ethyl acetate. The solution was applied directly to the sample surface (20mm^2) of an aluminum probe and crystallized on the surface after normal air drying.

All the mass spectra were obtained using our custom built time-of-flight mass spectrometer. The sample probe was introduced into the instrument through a fast pump-down load-lock antechamber. Our previous papers provide a detailed description of the instrument [4].

A pulsed ultraviolet laser with the wavelength of 266nm was used for desorption and ionization. The 8 ns duration ionization pulses were produced by attenuating the fourth harmonic of a Spectra-Physics Quanta Ray DCR-3Nd:YAG laser. The laser energy was $\sim 0.8 \times 10^7 \text{W/cm}^2$ at the focus. Each mass spectrum is the sum of fifty-five laser shots at a 5 Hz repetition rate.

The ion source optics are composed of the repeller, the extractor and accelerator plates based on Wiley-McLaren design. Switching the polarity on the ion source plates can produce mass spectra of either positive or negative ions. In the positive ion mode, the potentials on each ion optics are: 7500v on the repeller, 2470v on the extractor, with the

accelerator and flight tube at ground potential. A microchannel plate (MCP) detector is set at the end of the 96 cm flight tube. A fast high-voltage transistor switch (HTS50-06 from Eurotek, Germany) is used to provide a 271 ns delay between the creation of the ions with the laser pulse and the application of the high voltage for extraction of the ions. The delayed extraction of the ions allowed time for prompt decay of metastable ions and yielded improved resolution.

Results and Discussion

The mass spectra of the two isomers given in Fig. 1 have several features in common. In negative mode (Fig. 1a and 1b), both isomers show a molecular peak with mass 246 and $[M-Na]^+$ peak with mass 223. The $[M-SO_3Na]^+$ anion with mass 143 is most intense because the carbon-sulfur bond is easily broken in the ionization process [6].

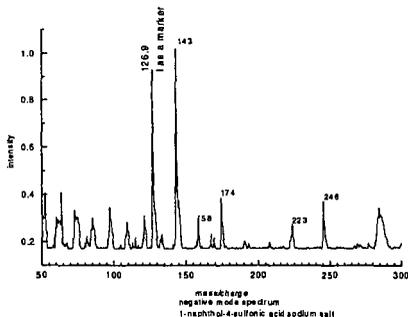


Fig. 1a

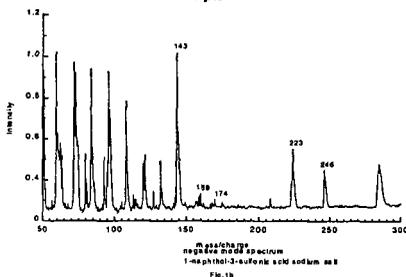
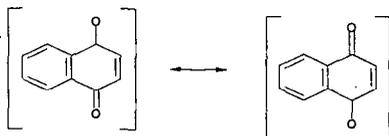
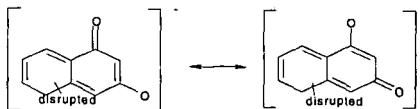


Fig. 1b

On the other hand, the two isomers did exhibit characteristic fragment ions in negative mode. The mass 158 anion is more stable in 1,4-SNS than in 1,3-SNS. The mass 158 anion is assigned as the naphthalene quinone anion, $[M-SO_2Na-H]^+$, following a dissociation path similar to that reported by Binkley et al. [7]. The sulfonate anions can rearrange in the gas phase reaction and form phenoxide ions. The enhanced signal intensity for the 1,4 isomer is driven by the charge delocalization. The 1,3 isomer cannot delocalize the negative charge as effectively.

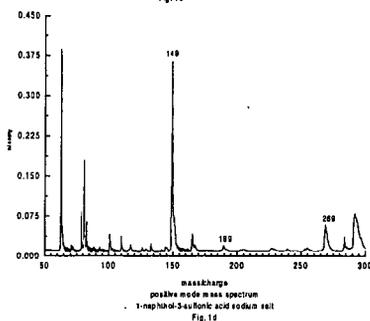
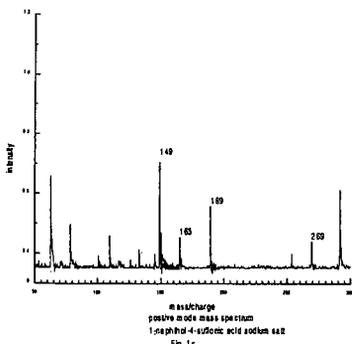


The 1,4-SNS forms quinone structure in which the negative charge is well distributed in the highly conjugated system



In 1,3-SNS the conjugate system is disrupted, therefore, the negative charge can not distribute as well as in 1,4-SNS. Therefore, the 158 anion is more stable in 1,4-SNS than in the 1,3-SNS.

Neither isomer forms a stable molecular positive ion, however diagnostic fragment ions are observed in Fig. 1c and 1d. Several sodium adduct ions are observed. The mass 269 peak, formed by association of Na^+ with the sulfonic acid salt, $[\text{M}+\text{Na}]^+$, is observed for both isomers. The Na^+ cation is the most intense peak due to the high vapor pressure of sodium and the low ionization potential.



The differences in the structure of the two isomers yields a difference in the positive ion spectra as well. The mass 189 cation is more intense in 1,4-SNS than in 1,3-SNS. The observation of Brykov et al. [8] that the 1,4 isomer can photochemically re-arrange in condensed phase or as a dimer pair to produce the 1,2 SNS isomer opens the possibility for a pathway that would produce the 189 cation. The 1,2 SNS isomer can form an epoxide adduct with Na^+ ions of mass 189.

Conclusion

In summary, the study of the 1,4-SNS and 1,3-SNS isomers provide new understanding of the fragmentation of the radical ions formed from hydrocarbon sulfates in gas phase. It demonstrates that slight change of molecular structure can cause differences in ion stability. The fragmentation pathways observed in mass spectrometry suggest that formation of naphthalene sulfonic acid in acidic sulfate aerosol droplets can lead to formation of naphthalene quinones by ultraviolet photochemistry.

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Chemical Composition of Fine Particles in the Tennessee Valley Region and Its Relationship to Stationary Sources

Roger L. Tanner, William J. Parkhurst, and Robert E. Imhoff
Tennessee Valley Authority
Atmospheric Sciences and Environmental Assessments Department
Muscle Shoals, AL 35662

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EXTENDED ABSTRACT

As the monitoring and regulatory implementation schedules for the revised particulate matter (PM) National Ambient Air Quality Standard (NAAQS) evolve, it is clear that the new annual NAAQS metric for fine particulate matter with aerodynamic diameter less than $2.5 \mu\text{m}$ ($\text{PM}_{2.5}$) will be difficult for many parts of the country to attain. The need to better understand the composition of fine particles ($\text{PM}_{2.5}$) and its temporal and spatial variability is broadly supported within regulatory, industrial and research communities. Realizing the potential consequences of the revised PM NAAQS, the Tennessee Valley Authority (TVA) and Tennessee Valley state and local regulatory organizations began operating the first comprehensive, regional prototype-FRM $\text{PM}_{2.5}$ monitoring network in the eastern U.S. on April 22, 1997^{1,2}. Every third-day $\text{PM}_{2.5}$ sampling was initiated at three core sampling stations in Nashville, Knoxville, and Lawrence County, TN. Five additional sites were added in Chattanooga and Memphis TN (August 1997), Decatur AL and Paducah KY (October 1997), and Huntsville, AL (June 1998).

The single-event particulate matter sampler models used in this effort included five prototype Partisol®-FRM Model 2000 (R&P Inc.) samplers, three prototype RAAS™ Model 2.5-100 (Graseby-Andersen) samplers, and one EPA-designated FRM $\text{PM}_{2.5}$ sampler, Model PQ200 (BGI Inc.). Each of these samplers draw air through a 10 micron (μm) size-selective inlet and remove particles greater than $2.5 \mu\text{m}$ with a WINS impactor. The $\text{PM}_{2.5}$ particles themselves were collected on Zefluor™ Teflon 46.2-mm filters with 2 mm pore size (Gelman Sciences, Inc.) through December 1998, thereafter on ID-stamped, Whatman filters with support rings. Initially, samples were collected for a 24-hour period every third-day; the sampling frequency was changed to every sixth-day on October 1, 1998.

Following gravimetric analysis (Mettler Microbalance), selected 24-hour samples were analyzed for elements Al through Pb using x-ray fluorescence (XRF) by EPA-approved Protocol 3. After XRF analysis, the samples were extracted ultrasonically and analyzed by the TVA's Support Services Group for ammonium by automated indophenol colorimetry and for sulfate and nitrate by ion chromatography. For selected sampling days at the network's core sites, samples of fine mass were collected on collocated samplers using quartz as the collection medium. These quartz filters were analyzed by the thermo-optical reflectance (TOR) technique³ for organic and elemental carbon. The filters were then extracted ultrasonically in water and analyzed for ammonium, sulfate, and nitrate as described above for Teflon filters. Data from the collocated Teflon & quartz samples were used to determine the average chemical composition of fine particles by season at the three core sites. Specific attention was given to seasonal variations in the fine particle chemical composition, and in composition differences between urban and rural sites.

During two additional periods, more intensive sampling was done at a mobile-source impacted site in Chattanooga, TN, about 3 km from the network site. Continuous measurements of mass (TEOM) and light scattering ($3\text{-}\lambda$ nephelometer) were made in early March, 1998, and repeated, with the addition of continuous elemental carbon measurements (aethalometer⁴), in September, 1998. The data from these measurements were used to examine diurnal and seasonal variations in mass and composition at this site. A new sampler (PC-BOSS⁵) designed to accurately measure both non-volatile and semi-volatile constituents of fine mass was tested at urban and rural sites to test the accuracy of the prototype FRMs. Our ongoing assessment of data from network and special studies allow us to provide preliminary answers to the following questions.

- *What are the fine particle mass concentrations in the South-central US and what are the implications relative to the NAAQS?* Fine particle annual mass concentrations in the Tennessee Valley range from 14 to 20 micrograms per cubic meter ($\mu\text{g}/\text{m}^3$). All seven urban/suburban sites exceeded the $15 \mu\text{g}/\text{m}^3$ level of the annual $\text{PM}_{2.5}$ standard. The rural Lawrence County TN site remained below the annual standard (Table). None of the stations exceeded the $65 \mu\text{g}/\text{m}^3$ level of the 24-hour $\text{PM}_{2.5}$ standard. Summer high-winter low seasonality is evident.

- *How well does the Federal FRM measure fine mass and what positive and negative biases does it have?* The current FRM PM_{2.5} mass measurements underestimate the contribution of volatile/semi-volatile nitrates and organic carbon species. Preliminary information from the summer of 1997 (PC-BOSS sampler) at our Lawrence County site indicates that the semi-volatile fraction is both highly variable and significant⁶. Since the organic fraction of fine particles appears to be highly suspect from a health effects standpoint, it is prudent to make periodic assessments of semi-volatile and non-volatile organic carbon fractions when particle composition measurements are made.
- *What is the composition of these fine particles and what do they imply for development of control strategies?* Based on composition measurements, both inorganic sulfate and carbonaceous compounds make up large fractions of PM_{2.5} mass (Figure). Sulfate provides the largest fraction (≈50%) in background air (Lawrence County) with organic carbon compounds making up next largest fraction (≈33%). For the urban stations the situation is largely reversed with the organic aerosol fraction being dominant (≈50%) followed by sulfate (≈30%). Control strategies designed to lower organic carbon (transportation and industrial sources) and sulfur dioxide emissions (fossil fuel combustion sources) will therefore be most effective in achieving compliance with the PM_{2.5} annual NAAQS.
- *What are the spatial, seasonal, and diurnal variations in these concentrations and what does this tell us about sources and fates?* Higher fractions of sulfate are found in fine particles at all sites in the summer months, compared to the remainder of the year. Diurnal variations show the effects of primary sources and meteorology, with higher concentrations of primary particles (e.g., elemental carbon) during the morning rush hour and higher concentrations of all constituents at the surface during periods in which a stable surface layer is present (poor vertical mixing).
- *What are the controllable fractions of fine mass and what are the sources of those potentially controllable fractions?* The largest fractions of fine mass are attributable to organic carbonaceous material and ammonium sulfates. The sulfate fraction can in theory be controlled by further reducing emissions of its gaseous precursor, SO₂, although non-linear gas-to-particle conversion processes appear to be reducing the "bang for the buck". The organic fraction is largely uncharacterized and a high priority should be placed on characterizing what fraction of it is controllable by reducing man-made emissions of particulate organics and their gas-phase precursors.

Table Monthly Mean PM_{2.5} Mass Concentrations (µg/m³). TN Valley PM_{2.5} Network

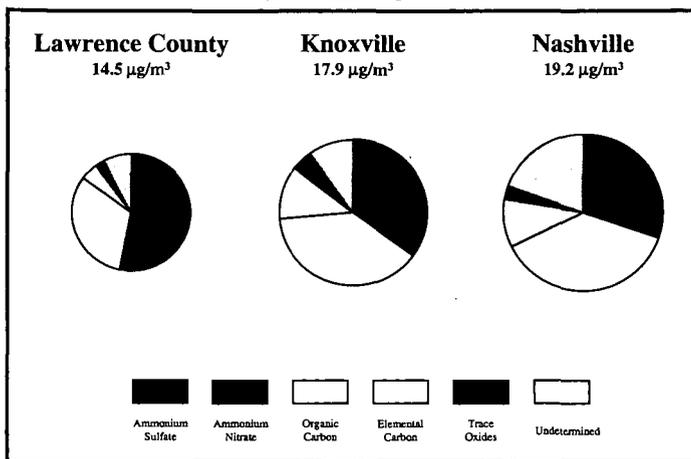
Month/Station	LC	KN	NS	CH	MP	DC	PD	HV	Mean
May-97	8.9	14.8	12.9						12.2
Jun-97	14.3	15.8	20.8						17.0
Jul-97	21.8	23.7	23.7						23.1
Aug-97	15.8	19.9	22.0	22.5					20.1
Sep-97	18.1	20.6	21.7	23.2	19.1				20.6
Oct-97	13.8	15.8	19.1	24.6	16.9	18.8	16.8		18.0
Nov-97	13.2	20.1	18.0	19.9	15.6				17.4
Dec-97	13.7	19.2	20.8	21.9	17.7	23.3	18.1		19.3
Jan-98	9.8	17.5	12.4	16.6	13.3		14.1		14.0
Feb-98	12.4	9.6	17.6	15.7	22.6		16.6		15.7
Mar-98	11.4	10.0	16.3	14.4	15.4	15.6	13.0		13.7
Apr-98	14.0	13.8	16.3	16.2	16.0	22.9	15.0		16.3
May-98	16.9	26.8	22.7	24.7	26.0	22.4	23.2		23.2
Jun-98	13.8	14.5	16.4	16.9	18.8	23.7	15.6		17.1
Jul-98	15.6	22.5	22.0	22.2	18.1	24.8	24.3	24.6	21.8
Aug-98	22.7	25.4	32.8	30.3	22.0	22.4	31.8	24.8	26.5
Sep-98	18.5	23.1	21.8	26.4	20.8		19.3	19.6	21.3
Oct-98	10.5	11.8	17.2	14.9	10.5		10.6	14.4	12.8
Nov-98	15.9	16.5	16.9	26.2	15.1		23.9	20.5	19.3
Dec-98	8.3	12.9	12.5	10.6	10.7		11.2	10.6	11.0
Jan-99	10.3	12.3	13.7	13.7	9.7		13.0	11.8	12.1
Feb-99	11.3	13.4	15.1	16.3	11.5		14.7	14.3	13.8
Mar-99	8.8		13.1	13.1	9.5		14.6	11.3	11.7
Apr-99	9.7		10.8	12.9			11.7	10.3	11.1
May-99	13.9			20.2			12.5	13.5	15.0
Jun-99	15.0			22.2			22.2	15.3	18.7
Station Mean	13.8	17.3	18.2	19.4	16.3	21.7	17.1	15.9	17.0

LC=Lawrence County TN, KN=Knoxville TN, NS=Nashville TN, CH=Chattanooga TN, MP=Memphis TN, DC=Decatur AL, PD=Paducah KY, HV=Huntsville AL.

Conclusions

TVA has measured fine particles ($PM_{2.5}$) in the Tennessee Valley region using prototype Federal Reference Method (FRM) samplers since April, 1997, and results indicate that compliance with the new NAAQS annual standard will be difficult. The chemical composition of fine particle samples has been estimated, and our results indicate that about 1/3 of the measured mass is sulfate, 1/3 is organic species, and the remainder is "other". The sulfate fraction is highest at rural sites and during summer months, with uniformly large fractions of organic aerosol in urban areas. Short-term variability of fine particle mass has been measured, and sampling performed which accounts for semi-volatile constituents of fine mass (nitrates, organics). Results show diurnal variability affecting exposure, and suggest that FRM measurements significantly underestimate organic constituents. Potentially controllable anthropogenic sources of fine particulate organics remain largely uncharacterized.

Figure $PM_{2.5}$ Composition



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SOURCING COAL COMBUSTION-DERIVED PAH IN THE ENVIRONMENT

Carole McRae^a, Cheng-Gong Sun^a, Clare F. McMillan^a, Colin E. Snape^a and Anthony E. Fallick^b

^aUniversity of Strathclyde, Department of Pure and Applied Chemistry, Glasgow G1 1XL, UK

^bScottish Universities Research & Reactor Centre, East Kilbride, Glasgow G75 0QU, UK

Keywords: Polycyclic aromatic hydrocarbons, coal combustion, source-apportionment.

ABSTRACT

To investigate the effects of domestic coal burning on the distribution and isotopic composition of environmental PAH, a series of soil samples were collected in a coal-burning village (Lochwinnoch) nearby Glasgow, UK. Analyses showed that, typically, PAHs in the Lochwinnoch samples were isotopically heavy having $\delta^{13}\text{C}$ values close to -25 ‰ that are consistent with the PAHs emanating from coal burning. It was also noted, however, that alkylated PAHs would appear to be more prominent in soot from coal fires than in the samples collected in Lochwinnoch where domestic combustion was determined to be the major source. Therefore, to address the possibility that parent PAHs may survive in soils preferentially, two weathering experiments have commenced using a low temperature coal carbonisation tar from the Coalite process. Initial results have shown that after as little as 80 days weathering period, parent PAHs, particularly fluoranthene and pyrene, become more prominent than the alkylated species, suggesting that parent PAHs survive oxidation/weathering to a greater extent than their alkylated counterparts.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAH) in the environment arise from a number of potential natural and anthropogenic sources, with major contributions from coal utilisation⁽¹⁾, diesel exhaust emissions⁽²⁾ and biomass combustion – both accidental and intentional⁽³⁾. Although conventional analytical techniques are useful for the identification and quantification of PAH in environmental samples, they provide little information on the source of these pollutants. The potential of using compound-specific isotopic analysis for source-apportionment of environmental PAH has been demonstrated by O'Malley *et al.*^(4,5), Lichtfouse *et al.*⁽⁶⁾ and the authors⁽⁷⁻¹⁰⁾. O'Malley *et al.* indicated that PAH arising from woodburning and vehicle emissions exhibited significantly different isotopic signatures⁽⁴⁾ and the same authors have also reported the isotopic compositions of *n*-alkanes and PAH produced from combustion of C₃ and C₄ plant species⁽⁵⁾. Lichtfouse *et al.*⁽⁶⁾ have reported significant anthropogenic hydrocarbon inputs into soil using a combination of biomarker, $\delta^{13}\text{C}$ and ^{14}C analyses. The authors have found that the $^{13}\text{C}/^{12}\text{C}$ isotopic ratios for PAH derived from coal and wood pyrolysis and diesel particulates vary over a range by ca. 8 ‰ which could provide a basis for source apportionment in a number of environments⁽⁷⁾.

To establish a basis for applying gas chromatography - isotope ratio mass spectrometry ($\delta^{13}\text{C}$ GC-IRMS) to source PAHs from coal utilisation, stable isotopic ratios have been determined as a function of coal rank and process conditions⁽⁸⁻¹⁰⁾. The results have indicated that the primary control on the isotopic values of coal-derived PAHs is the extent of ring growth required to form PAHs during processing. Thus, for relatively mild conversion processes such as low temperature carbonisation where the major aromatics are alkyl substituted 2-3 ring PAHs, the isotopic signatures are similar to those of the parent coals (ca. -25 ‰). However, the $\delta^{13}\text{C}$ values for the PAHs become lighter in going to high temperature carbonisation, gasification and fluidised-bed combustion as the extent of ring condensation increases and confirming that the PAHs are not released as primary volatiles. To demonstrate the applicability of the technique to the analysis of environmental PAHs where major inputs from coals could be expected, samples collected in the vicinity of a low temperature carbonisation plant in the UK were analysed^(9,10). In addition to low temperature coal tar, significant inputs of PAHs from transport fuels, high temperature carbonisation and combustion sources (coal/biomass) were inferred from the isotopic ratios, taken in conjunction with the differences in alkyl substitution patterns.

In this paper we report findings on PAH formation in domestic (grate) combustion and resultant isotopic compositions. Furthermore, to trace PAH from domestic combustion, a series of soil samples have been collected in the area of Lochwinnoch, a village approximately 15 miles south west of Glasgow, UK, where a large proportion of the domestic properties still use coal combustion as a primary source of heating. To determine the fate of PAH following emission to the environment, an experiment has commenced using soil spiked with low

temperature coal carbonisation tar from the Coalite process^(9,10) to investigate the effect of biodegradation/weathering on PAH survival and their resultant isotopic compositions.

EXPERIMENTAL

Three domestic soot samples were selected for analysis. The first sample (domestic fire soot 1) emanates from a single coal-burning fire chimney and the sample supplied by a local chimney sweep also comes from a series of fires burning only coal. However, the second soot sample (domestic fire soot 2) is from a domestic fire on which both coal and wood have been burned. Soil samples were collected from various points in the village of Lochwinnoch, 15 miles south west of Glasgow, UK. Collection sites encompassed areas the village Main Street (sample LW5), the centre of a residential area of the village (sample LW6) and a sample collected from a heritage trail approximately 1 mile from the centre of the village (sample LW7).

Soil from open ground approximately 1 mile from Glasgow city centre was dried at 40 °C *in vacuo*, and the soil sample was then mixed with a predetermined quantity of low temperature coal tar (20 % w/w). The coal tar-coated soil was divided into sub-fractions that were placed where the original soil sample was collected. Each sub-fraction was packed in a roughly cylindrical area to a depth of approximately 2 cm and diameter of 6 cm (the beds for each sub-fraction were approximately 3 cm apart). The sub-fractions have been recovered after increasing periods of time. By the time the second sample was taken (80 days), grass growth was already evident over the coal tar coated soil.

All soil and soot samples were dried *in vacuo* at 40°C, soil samples ground to 75-212 µm particle size and all samples (including tar pre-coated soil) extracted by reflux in dichloromethane (DCM) for 10 hours. The DCM extracts (following solvent removal) were fractionated by open column alumina chromatography (fine grain activated neutral alumina) to yield neutral aromatic fractions for $\delta^{13}\text{C}$ GC-IRMS analysis as described previously^(7,8,10). Reported isotopic data represent the arithmetic means of at least two duplicate analyses and the estimated repeatability for individual hydrocarbons, based on an earlier study by Eakin *et al*⁽¹¹⁾ with the VG Isochrom II GC-IRMS system, is 0.2-0.4 %. The experimental error of the machine was between 0.5 and 1.0 ‰, with precision decreasing as the intensity of GC peaks, in relation to the unresolved background, decreased.

RESULTS AND DISCUSSION

Domestic Soot Samples

Figure 1 compares the gas chromatograms for the neutral aromatics extracted from the domestic soot samples. The isotopic compositions of extracted PAH for 2 of the samples are listed in Table 1. The sample provided by the chimney sweep emanates from coal fires as does soot sample number 1 (collected from a single chimney). However, domestic soot sample number 2 was obtained from the chimney of a domestic fire on which both coal and wood have been burned. The parent PAHs in sample 2 are much more dominant than in the other two samples (Figure 1) and their $\delta^{13}\text{C}$ values are in the region of -28 to -30 ‰. As can be seen from Table 1, the isotopic compositions of PAH extracted from soot sample number 1, where coal is known to be the sole contributor, lie in the region of -25 ‰. Since UK bituminous coals are known to exhibit bulk isotopic compositions in the region of -24 to -25 ‰^(9,10), this would suggest that PAH released are primary volatiles from coal devolatilisation. By considering these isotopic compositions and also taking account of the fact that wood burning gives PAHs with values below -30 ‰⁽⁷⁾, it can be suggested that, in this instance, the PAHs in domestic soot sample number 2 have been sourced from both coal and wood. The parent PAHs are more dominant in the soot provided by the chimney sweep than in the first domestic sample analysed, but alkylated PAHs are still major constituents (Figure 1). Comparison of the two coal-burning chimney samples suggests that the ratio of alkylated to parent PAHs varies considerably in soot from domestic fires and is clearly going to reflect the average devolatilisation temperature. The authors are now conducting tests under controlled conditions on both bituminous coals and smokeless fuels to further examine this phenomenon.

Lochwinnoch Soil Samples

Figure 2 shows the gas chromatograms for the neutral aromatics extracted from the Lochwinnoch soil samples investigated and Table 2 lists the $\delta^{13}\text{C}$ values of selected PAHs and the neutral aromatic yields for each of the samples. A full suite of samples have been analysed by GC, but the 3 samples selected for GC-IRMS exemplify the variations found in composition. Sample LW5 was collected from the village Main Street and, as well as the parent PAH peaks, a broad unresolved hump is also evident in the chromatogram. This is characteristic of the highly complex distribution of heavily substituted alkyl aromatics found in diesel particulates^(7,9,10). The

sample collected from a residential street (LW7) displays a similar distribution of parent PAH as the main street sample, but the broad shoulder arising from heavily substituted alkyl aromatics is much less prominent in the chromatogram (Figure 2), suggesting a lower input from diesel particulate. A sample was also collected from a heritage trail situated approximately one mile from the centre of the village (LW 6), which displays a different distribution of parent PAH to the other two samples. As can be seen from Table 2, the total concentration of neutral aromatics in the heritage trail sample (0.02 %) was also significantly lower than corresponding concentrations in the residential street sample (0.08 %) and the main street sample (0.2 %).

The $\delta^{13}\text{C}$ values for the parent PAH are generally quite similar for samples LW5 and LW7 and mainly occur in the range -24 to -26 ‰, consistent with the PAHs arising from domestic coal burning. However, alkylated aromatics are much less prominent in the residential street sample (LW7) than the soot samples obtained thus far from coal fires (cf. Figures 1 and 2). The slightly heavier values (ca. -24 ‰) for the lower molecular mass PAH in the main street sample (LW5) could be indicative of biodegradation/weathering having occurred to a greater extent in relation to LW7. The distribution of parent PAHs in the Heritage Trail sample (LW6) is significantly different to that for the other two samples. Further, the higher molecular mass PAHs and phenanthrene/anthracene are isotopically light (-29 to -30.5 ‰) suggesting an input from sources other than coal and diesel. The location of the Heritage Trail sample in conjunction with the isotopically light PAH would suggest an input from biomass combustion.

Weathering experiment

The GC traces of the neutral aromatics from the initial low temperature tar and the tars recovered after the soil had been in the ground for 40 and 80 days are compared in Figure 3. After 40 days, the lower molecular mass constituents (alkylnaphthalenes) decreased to a considerable extent and, after 80 days, the proportions of parent PAHs remaining, notably fluoranthene and pyrene, are beginning to increase in relation to the complex distribution of alkylated aromatics whose peaks dominate the GC trace for the initial tar. Thus, these preliminary results appear to provide direct evidence that, even after a relatively short weathering period, the alkylated aromatics are beginning to be depleted preferentially in relation to the parent PAHs.

CONCLUSIONS

The PAHs in the Lochwinnoch village samples were isotopically heavy having $\delta^{13}\text{C}$ values close to -25 ‰ that are consistent with the PAHs emanating from coal burning. The sample collected from a trail outside the centre of the village exhibited a different distribution of PAH to those collected on the main street and residential area. However, alkylated PAHs appear to be more prominent in soot from coal fires than in the samples collected in Lochwinnoch where domestic combustion was determined to be the major source. Initial results from a weathering experiment show that after as little as 80 days, parent PAHs, particularly fluoranthene and pyrene, become more prominent than alkylated species, suggesting that these compounds may survive biodegradation to a greater extent than their alkylated counterparts.

ACKNOWLEDGEMENT

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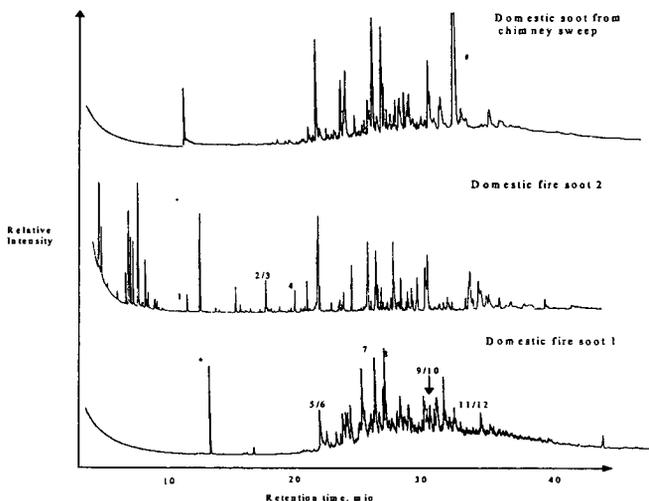


Figure 1 GC traces for the aromatics from the domestic soot samples
 Key 1. Naphthalene; 2. Acenaphthylene; 3. Acenaphthene; 4. Fluorene; 5. Phenanthrene; 6. Anthracene; 7. Fluoranthene; 8. Pyrene; 9. Benz(a)anthracene; 10. Chrysene; 11. Benzo(b)fluoranthene; 12. Benzo(k)fluoranthene; 13. Benzo(a)pyrene; 14. Dibenzo(a,h)anthracene; 15. Benzo(ghi)perylene; 16. Indeno(1,2,3)pyrene; * Internal standard; #plasticiser

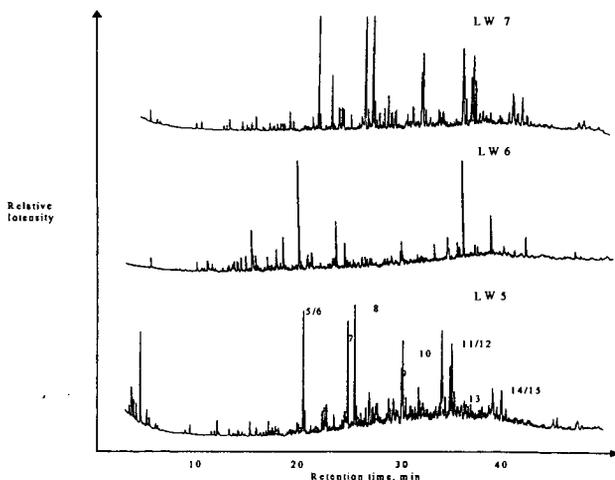


Figure 2 GC traces for aromatic fractions from Lochwinnoch samples
 Key 5. Phenanthrene; 6. Anthracene; 7. Fluoranthene; 8. Pyrene; 9. Benz(a)anthracene; 10. Chrysene; 11. Benzo(b)fluoranthene; 12. Benzo(k)fluoranthene; 13. Benzo(a)pyrene; 14. Dibenzo(a,h)anthracene; 15. Benzo(ghi)perylene; * Internal standard.

Table 1 Isotopic compositions of PAH extracted from domestic soot samples

PAH	Soot 1	Soot 2
Phenanthrene	-24.8	-29.0
Anthracene	-25.5	-28.9
Fluoranthene	-25.9	-30.6
Pyrene	-26.1	-28.9
Benzo(a)anthracene	-25.2	-29.5
Chrysene	-25.2	-29.4
Benzo(a)fluoranthene	-24.2	-29.4
Benzo(k)fluoranthene	-24.5	-29.5

Table 2 Neutral aromatic yields and isotopic compositions of PAH extracted from Lochwinnoch samples

PAH	Sample/Isotopic Composition (%)		
	LW 5	LW 6	LW 7
1. Naphthalene	-24.6	-	-
2. Acenaphthylene	-	-	-25.0
3. Acenaphthene	-	-	-25.0
4. Fluorene	-23.9	-25.1	-25.8
5. Phenanthrene	-23.7	-29.1	-25.6
6. Anthracene	-23.7	-29.1	-28.1
7. Fluoranthene	-24.7	-25.0	-25.1
8. Pyrene	-25.3	-25.2	-25.7
9. Benzo(a)anthracene	-24.7	-26.0	-26.0
10. Chrysene	-24.7	-26.0	-26.0
11. Benzo(a)fluoranthene	-25.2	-30.5	-25.7
12. Benzo(k)fluoranthene	-25.2	-30.5	-25.7
13. Benzo(a)pyrene	-25.3	-30.5	-26.8
Neutral aromatic yield (%)	0.21	0.02	0.08

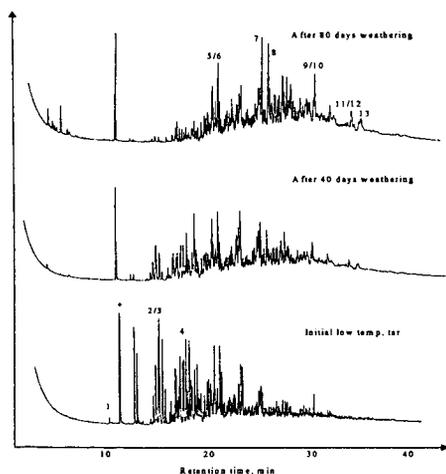


Figure 3 GC traces for aromatic fractions from the coal tar and soil extracts after 40 and 80 days
 Key 1. Naphthalene; 2. Acenaphthylene; 3. Acenaphthene; 4. Fluorene; 5. Phenanthrene; 6. Anthracene; 7. Fluoranthene; 8. Pyrene; 9. Benzo(a)anthracene; 10. Chrysene; 11. Benzo(b)fluoranthene; 12. Benzo(k)fluoranthene; 13. Benzo(a)pyrene; *Internal Standard.

AMBIENT FINE PARTICULATE MATTER (PM_{2.5}) SAMPLING AND ANALYSIS IN THE UPPER OHIO RIVER VALLEY

Robinson P. Khosah, Terence J. McManus and Robert O. Agbede
Advanced Technology Systems, Inc., 639 Alpha Drive, Pittsburgh, PA 15238

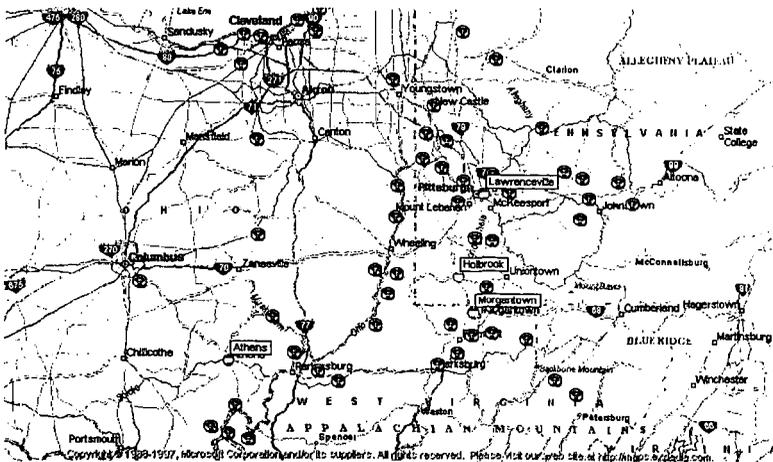
Thomas J. Feeley, III
U. S. Department of Energy
Office of Fossil Energy/Federal Energy Technology Center, Pittsburgh, PA 15236

INTRODUCTION

Ambient fine particulate matter (PM_{2.5}) originates from a wide variety of emission sources, both man-made and natural. The combustion of coal to generate electricity can produce primary PM_{2.5} (e.g., fly ash, carbon soot, associated trace metals), the gaseous precursors (e.g., SO₂ and NO_x) to the formation of secondary fine particles (e.g., ammonium sulfates and nitrates), and condensable species (e.g., H₂SO₄). However, there remain numerous uncertainties regarding the linkage between coal-fired boiler emissions and the visibility and health-related impacts that have been associated with ambient fine particulates. As part of its ambient fine particulate program, the DOE-Federal Energy Technology Center (DOE-FETC), in cooperation with key stakeholders including EPA, local and state environmental agencies, industry, and academia, established and is operating several PM_{2.5} speciation sites in the Upper Ohio River Valley (UORV).

The overall goal of the Upper Ohio River Valley Project (UORVP), is to investigate the nature and composition of fine particulate (PM_{2.5}) and its precursor gases in the Upper Ohio River Valley and provide a better understanding of the relationship between coal-based power system emissions and ambient air quality in the Upper Ohio River Valley region. This geographical area, encompassing southeastern Ohio, western Pennsylvania, and northwestern West Virginia, was chosen for this extensive fine particulate research because it mirrors an area in the eastern half of the continental United States that is not well characterized but has a high density of coal-fired electric utility, heavy industry (e.g., coke and steel making), light industry, and transportation emission sources. The UORV is also in the center of the ozone transport region, which provides a platform to study interstate pollution transport issues. This region, with its unique topography (hills and river valleys) as well as a good mix of urban and rural areas, has a high population of the elderly who are susceptible to health impacts of fine particulate as well as other related environmental issues (e.g., acid rain, Hg deposition, ozone).

Advanced Technology Systems, Inc. (ATS), with Desert Research Institute (DRI) as the subcontractor, was contracted by DOE-FETC in September 1998 to manage the UORVP. The map below shows the location of the sites.



Two urban and two rural monitoring sites are included in the UORVP. The four sites selected were all part of existing local and/or state air quality programs. One urban site is located in the Lawrenceville section of Pittsburgh, Pennsylvania. This site is an air quality monitoring station operated by the Allegheny County Health Department. A second urban site is collocated at a West Virginia Division of Environmental Protection (WVDEP) monitoring station at the Morgantown, West Virginia, Airport. One rural site is collocated with the Pennsylvania Department of Environmental Protection (PADEP) at a former NARSTO-Northeast site near Holbrook, Greene County, Pennsylvania. The other rural site is collocated at a site operated by the Ohio Environmental Protection Agency (OHEPA) and managed by the Ohio State Forestry Division in Gifford State Forest near Athens, Ohio.

EXPERIMENTAL

Testing and Analysis Plan

Table 1 provides the overall PM_{2.5} sampling and analysis plan requirements.

The UORVP is arranged to obtain a base level of intermittent samples every sixth day at all the four sites. This will allow for estimates of monthly, seasonal, and annual averages. To investigate the differences between months of high production of secondary particulates from atmospheric reactions, one month in the summer will be used for sampling every day, with PM_{2.5} material obtained on a 6-hour schedule to evaluate episodal and diurnal variations in sample composition. Sampling for particulate (ammonium) nitrate and gaseous nitrogen species, as well as ammonia, will provide data to investigate the apparent low nitrate levels found in eastern PM_{2.5} catches.

For comparison with summer conditions, a one-month daily sampling period was performed in February 1999 and another is projected for mid-winter 2000. To provide for comparability with stations to be set up as part of the national PM_{2.5} monitoring network, the basic sampling is being conducted using PM_{2.5} FRM sequential filter-based samplers. In addition, PM₁₀ sequential samplers were installed at one urban and one rural site. The UORVP sampling protocol will allow for a comparison of the PM₁₀ and PM_{2.5} mass and chemistry, but the emphasis of the project is on the PM_{2.5} component.

The measurement of several gases that are relevant to characterizing photochemistry, or are precursors for particle formation, was also implemented. These include ozone and its precursors (NO_x, HNO₃, and NH₃) as well as sulfur dioxide (SO₂). The observations will be completed with the acquisition of surface meteorological data at all sites, including wind speed and direction, temperature, relative humidity, precipitation, and UV radiation and insolation.

ATS contracted DRI and LabCor to analyze the collected samples following the guidance presented in Table 1.

RESULTS AND DISCUSSION

For brevity reasons, only a sample of the results obtained during the month of June 1999 are shown in Table 2. The continuous trace depicts thirty-minute average ambient air particulate loadings obtained with a PM_{2.5} tapered element oscillating microbalance (TEOM) with measurement initiating after midnight of May 31. Besides showing emission trends that peak around midday, the data shows that although the average loading is around 10 to 20 µg/scm, levels as high as 75 µg/scm are evident. The bars shown at intervals represent 24-hour averages for the TEOM (bottom bar) compared to discrete filter 24-hour integrated mass loadings (top bar). Please note that when the values agree closely, the bars are fused into one as indicated by the average values from June 29. These data provide a snapshot of how well the TEOMs and the discrete filter samplers are performing.

CONCLUSIONS

The goal of this project is to obtain and document reliable and quality data pertaining to ambient fine particulate along the Upper Ohio River Valley. The data obtained should:

- Provide generalized idea of types of PM_{2.5} sources.
- Provide input on the impact of sampling artifacts such as condensation/volatilization on FRM performance.
- Provide various correlations (day/night, urban/rural, etc).

- Provide information on $PM_{2.5}$ concentrations/compositions for a part of the country not previously characterized.
- Provide a data base for others to use for:
 - Health studies
 - Source/Receptor analysis
 - Management System Development and
- Provide a platform for further scientific research.

The sample data discussed above confirms that reliable data that can be duplicated by two different sampling techniques is being obtained. Further data reduction, analysis, correlation and interpretation are on going and will be presented at the conference.

ACKNOWLEDGEMENTS

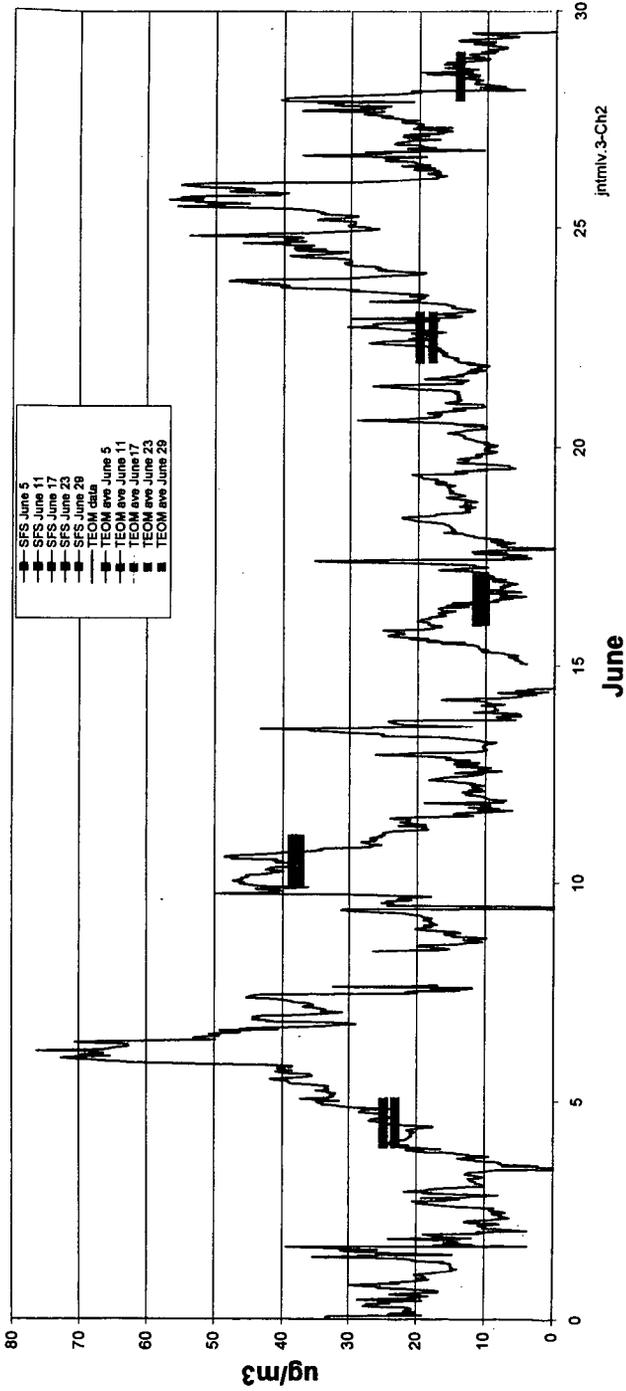
We wish to acknowledge DOE-FETC funding on Contract No. DE-AC26-98FT40456 and Dcsert Research Institute, University of Ohio at Athens, and LabCor as subcontractors.

Table 1 - PM_{2.5} SAMPLING AND ANALYSIS

SAMPLER	DENUDER	CHANNEL NO.	FILTER MATERIALS		ANALYSIS	
			Front	Back	Front	Back
SPS-PM2.5	(none)	A	Teflon*	Quartz	Mass (Gravimetry), Elements (XRF)	Carbon (TOR)
		B	Quartz	Cellulose/NaCl	Carbon (TOR); O ₃ ; NO _x ; SO ₂ ^a ; (IC); NH ₄ ⁺ ; (AG); Na ⁺ ; K ⁺ ; (AA)	NO _x ; (IQ)
SASS #72	(none)	A	Teflon*	Quartz	Mass (Gravimetry), Elements (XRF)	Carbon (TOR)
		B	Quartz	Cellulose/NaCl	Carbon (TOR); O ₃ ; NO _x ; SO ₂ ^a ; (IC); NH ₄ ⁺ ; (AG); Na ⁺ ; K ⁺ ; (AA)	NO _x ; (IQ)
SPS-PM10	(none)	A	Teflon*	Quartz	Mass (Gravimetry), Elements (XRF)	Carbon (TOR)
		B	Quartz	Cellulose/NaCl	Carbon (TOR); O ₃ ; NO _x ; SO ₂ ^a ; (IC); NH ₄ ⁺ ; (AG); Na ⁺ ; K ⁺ ; (AA)	NO _x ; (IQ)
SGS-TP	Nitric Acid (none)	A	Quartz	Cellulose/NaCl	NO _x ; (IQ)	NO _x ; (IQ)
		B	Quartz	Cellulose/NaCl	NO _x ; (IQ)	NO _x ; (IQ)
SASS #74	Nitric Acid (none)	A	Quartz	Cellulose/NaCl	NO _x ; (IQ)	NO _x ; (IQ)
		B	Quartz	Cellulose/NaCl	NO _x ; (IQ)	NO _x ; (IQ)
SGS-PM2.5	Ammonia (none)	A	Quartz	Cellulose/Citric Acid	NH ₄ ⁺ ; (AG)	NH ₄ ⁺ ; (AG)
		B	Quartz	Cellulose/Citric Acid	NH ₄ ⁺ ; (AG)	NH ₄ ⁺ ; (AG)
SASS #75	Ammonia (none)	A	Quartz	Cellulose/Citric Acid	NH ₄ ⁺ ; (AG)	NH ₄ ⁺ ; (AG)
		B	Quartz	Cellulose/Citric Acid	NH ₄ ⁺ ; (AG)	NH ₄ ⁺ ; (AG)
FRM (R&EP) ^a	(none)	-	Teflon*	(none)	Mass (Gravimetry), Elements (XRF)	-
FRM (R&EP) ^b	(none)	-	Quartz	(none)	Carbon (TOR); O ₃ ; NO _x ; SO ₂ ^a ; (IC); NH ₄ ⁺ ; (AG); Na ⁺ ; K ⁺ ; (AA)	-
Portable PM2.5	(none)	-	Polycarbonate	(none)	COSEM	-

XRF = X-Ray Fluorescence, TOR = Thermal/Optical Reflectance, IC = Ion Chromatography, AC = Automated Cobinometry, AA = Atomic Absorption, COSEM = Computer Controlled Scanning Electron Microscopy

TABLE 2: Lawrenceville-TEOM PM2.5 & SFS PM2.5



RAPID, MEASUREMENT-BASED SOURCE APPORTIONMENT OF AIR PARTICULATE MATTER

Henk L.C. Meuzelaar¹, Jacek P. Dworzanski¹, SucAnne N. Shcya¹, Sun Joo Jeon¹, JoAnn
Lighty², Adel F. Sarofim² and Gerardo M. Mejia Velazquez³

¹ Center for Micro Analysis and Reaction Chemistry

² Department of Chemical and Fuels Engineering

University of Utah

Salt Lake City, UT 84112

³ Center for Environmental Quality

ITESM

Monterrey, N.L., Mexico

KEYWORDS: air particulate matter characterization, source apportionment, thermal desorption GC/MS.

INTRODUCTION

There are two basic approaches to the quantitative apportionment of air particulate matter (PM) source contributions at a given receptor site and point in time. The first approach is based on a detailed inventory of the contributing local and long range sources and their expected PM emission activities (at the selected point in time minus the calculated transport time), combined with the use of atmospheric dispersion models capable of calculating the probability that particulate matter emitted by a given source will be transported to the selected receptor site at that particular point in time. The second approach is based on detailed physical and chemical characterization of one or more PM samples collected at the selected receptor site and time point, combined with the use of quantitative receptor models capable of apportioning these characteristics to potential local and long range sources with the aid of a library of known source patterns.

As pointed out in many textbooks [1], both approaches should be combined whenever feasible. In practice, however, most PM source apportionment efforts cannot draw upon reliable source emission and activity inventories and are also severely constrained by the high cost and time requirements of comprehensive PM characterization efforts. As a result, our present knowledge about the relative contributions of local and long range PM sources to air quality problems within many North American airsheds, let alone airsheds in other areas of the world, provides an inadequate basis for effective regulatory measures aimed at cost-effective protection of health and environment. Consequently, there is a need for the development of rapid, reliable and cost-effective PM characterization and apportionment techniques.

Currently used characterization methods for PM receptor samples are typically based upon inorganic analysis of 24-hr filter samples by means of x-ray fluorescence (XRF), proton-induced x-ray emission (PIXE), scanning electron microscopy with energy dispersive x-ray analysis (SEM-EDAX), or neutron activation analysis (NAA) methods. Over the past decade organic PM characterization methods involving solvent extraction of 24-hr filter samples followed by combined gas chromatography and mass spectrometry (SX-GC/MS) have demonstrated their power in providing hundreds of potential source marker compounds, particularly for a wide range of petroleum- and biomass-type materials combustion and processing sources which fail to produce characteristic inorganic markers or patterns. Quantitation of organic as well as inorganic measurements is typically achieved on the basis of mass balance techniques involving careful weighing of moisture-equilibrated filters (before and after exposure) and expressing chemical parameters in percentage of total sample mass.

Over the past few years, the advantages of novel PM sampling and analysis methods requiring only 1- to 2-hr long sampling periods, thereby producing time-resolved circadian PM profiles revealing characteristic anthropogenic activity and/or meteorology cycles as well as episodic events, were demonstrated for selected organic PM marker components by some of the present authors [2] using thermal desorption (TD) GC/MS techniques. Equally fast sampling approaches to inorganic PM characterization by means of SEM-EDAX and PIXE were demonstrated by Anderson et al. [3]. Although use of these novel, rapid sampling methods can greatly speed up source attribution, quantitative source apportionment still requires laborious filter weighing operations. Moreover, in areas with new or unusual sources and fuels, existing source profiles are often inadequate, thus requiring lengthy, costly and socio-politically sensitive source sampling and characterization operations.

A novel, rapid PM characterization strategy is presented. The procedures outlined can drastically reduce the time and effort required for exploratory source apportionment studies and are based on a combination of: (1) rapid TD-GC/MS of 2-hr PM samples; (2) differential source plume profiling of complex sources or source clusters; and (3) real-time, size-distributed particle concentration measurements.

EXPERIMENTAL

PM samples for TD-GC/MS analysis were collected on 19 mm dia. quartz fiber (QF) filters in a 16.7 l/min flow of air passing through an isokinetic (dichotomous sampler type) ambient air sampling tower equipped with a 10 micrometer cut-off impactor. QF filters were cleaned by preheating in a high temperature furnace and stored in particle-free containers, as described by Sheya et al. [4]. QF slivers of approximately 2 mm wide were reproducibly cut from the particle-laden filters and inserted into carefully cleaned borosilicate glass sample tubes and quickly inserted in to the hot (250 C) injection port of a GC system (HP 5890A) equipped with a 10 m long, 320 micrometer i.d. GC column coated with an 0.25 micrometer layer of DB1 and connected to a desk-top quadrupole mass spectrometer (HP MSD5972). When rapid heating of the QF slivers to higher temperatures is desired, e.g. for pyrolysis studies, the pyrex tubes can be lined with ferromagnetic foils of precisely known inductive heating behavior and a well-defined end point temperature corresponding to the Curie-point temperature of the selected alloy.

GC/MS data were analyzed using the HP ChemStation program and NBS mass spectral library. Multivariate statistical analysis of relative peak intensity data, as well as the corresponding size-distributed particle count and meteorology data where applicable, was performed by means of principal component analysis (PCA) using the NCSS version 7.0 software package, followed by Varimax rotation of the PCA loadings and scores to highlight the more highly orthogonalized components in PCA space. Where appropriate, the scores of the first four Varimax factors were plotted in the form of time-resolved "skyline" plots using standard plot programs.

Size-distributed particle concentration measurements were performed with a Climet Model CI 208C 8-channel particle analyzer with specially built computer interface. Total particle volumes in each size range were calculated assuming distribution-corrected average particle sizes and spherical particle shapes.

RESULTS AND DISCUSSION

Figure 1 shows the close agreement between TD-GC/MS and SX-GC/MS analysis profiles of PM samples obtained from the same Hi-Vol quartz fiber filter. In studies currently underway in our laboratory of the nearly 100 compound peaks routinely monitored in the GC/MS profiles approximately 90 % are readily identifiable in both profiles, with the intensities of most of these showing strong correlations. Clear differences are seen in the broad multimodal "humps" underlying both profiles. These humps, generally referred to as the unresolved complex matter (UCM), are highly characteristic of the GC/MS profiles of both solvent and thermal extracts from PM receptor samples and are also seen in most combustion source samples. Apparently, the physicochemical differences between both extraction methods result in somewhat different relative UCM fraction yields. Presumably, for the SX-GC/MS method these relative UCM fraction yields will also be affected by the choice of the solvent whereas the relative UCM yields of the TD-GC/MS technique may well vary as a function of desorption conditions. Thus far, the observed differences appear to be quantitative rather than qualitative and, thus, should be amenable to routine standardization and calibration procedures.

The type of information obtainable from time-resolved circadian TD-GC/MS profiles is illustrated by the skyline plots shown in figure 2. Rather than to show an arbitrary selection of the many different single compound profiles produced by this technique each skyline plot in figure 2 shows a linear combination ("factor") of highly correlated compound profiles, thought to represent a particular PM 10 source, or combination of related sources. To further illustrate the validity of the factor analysis approach to source detection, also commonly used to reduce and interpret inorganic PM10 compound data [5], the same type of factor loading patterns producing the factor score profiles shown in figure 2 (representing a series of PM10 samples collected at the international bridge in Hidalgo, at the USA/Mexico border in December 1995) was found in two other sets of samples obtained at the border in different locations and at different time periods in December. As expected, combustion sources known to produce significant organic PM emissions are dominant. However, the prominent (5 sigma) "urban dust" event observed in the evening of December 6th is largely characterized by inorganic, re-entrained city dust components but can still be observed thanks to several characteristic organic markers [6].

Since weighing of 2-hr filter samples would not only be very time-consuming but is also impractical in view of the more than 10x lower average sample quantities (compared to conventional 24-hr samples), a different approach needs to be found to calibrate each sample with regard to differences in sample size as a basis for quantitative compound analysis by TD-GC/MS. This is achieved by the use of multichannel (size-distributed) particle counting in parallel with the collection of each 2-hr filter sample, thus allowing us to calculate the number of particles collected by the filter in each size category. As shown in figure 3, the four upper and the four lower channels of an 8-channel optical particle counter (OPC) track each other closely with regard to relative changes in calculated total particle counts. Between these two sets of channels, however, significant quantitative as well as qualitative differences can be observed. On several occasions we have been able to correlate calculated total particle volumes (assuming spherical particle shapes for the purpose of convenience) with PM mass measurement data obtained with nearby situated Beta-gauge instruments. An example of the close agreement achievable using a simple, single shape plus density correction coefficient is shown in figure 4. Both weighing and size-distributed counting techniques have their potential strengths and weaknesses as book-keeping ("balancing") methods for PM samples and their components, as non-correctable losses and gains in particle numbers as well as in total particle mass can occur on the filter during and after collection. A detailed discussion of these pros and cons falls outside the page limitations of these preprints but some relevant data will be presented in the talk. It should be noted that each particle size-distribution profile is a vector unto itself. Consequently, substitution of particle count vectors for mass numbers in source apportionment methods such as the widely used chemical mass balance (CMB) model, requires some adaptation of the algorithms to higher dimensional outputs, e.g. by substituting partial least squares or canonical correlation analysis methods for the conventional multilinear regression method.

Finally, we need to examine the possibility of by-passing the conventional source sampling and characterization methods, requiring the use of elaborate equilibrium chambers permitting direct stack, flue or tailpipe sampling of individual sources. Although these methods are likely to remain indispensable for large comprehensive source characterization studies, conceptually the main difference with ambient source plume samples taken in close proximity to the source is the inevitable dilution with ambient air containing background PM. However, more than likely the source is using plenty of intake air with background PM (which may or may not be altered during its passage). This intake air background can usually be ignored in the source profile because of the very high concentrations of emitted particulates. However, these high concentrations, often accompanied by above ambient temperatures and particle flow velocities, come at a high cost since the concentration, size distribution and composition of the sampled particles may be affected by various non-equilibrium processes.

When obtaining ambient plume samples in close proximity to the source the advantages of more highly representative particle equilibria are now being traded off for the disadvantages of higher dilution and additional contamination with background PM. Thus, it will largely depend on the sensitivity and specificity of the analytical methods used to obtain the needed PM source profiles whether this trade-off is acceptable or not. As shown by the factor analysis examples in figure 2 the large numbers of highly specific variables in GC/MS based methods enables successful linear deconvolution of complex mixture profiles into their chemical components. Based on hands-on experience we expect relatively few problems in subtracting background contributions from targeted source profiles as soon as the contribution of the targeted source, or source cluster, accounts for more than 20-30 % of the total PM signal.

In order to verify both the ambient equilibrium conditions of the source PM components, the nature and concentration of background PM components and the rate of dilution it will be advantageous to obtain control samples and size-distributed particle count measurements directly upwind of the source (or source cluster) as well as further downwind inside the plume. Of course, the proposed approach will not work well with source (cluster) plumes which are too high above ground to be sampled conveniently at a reasonable distance from the source (cluster) and will also be strongly dependent upon favorable weather conditions.

Figure 5 provides a purely conceptual example of the combined use of differential source plume profiling and size-distributed particle volume balancing as a way of determining the quantitative relationship between the intensities of observed chemical source markers (or marker pattern) in receptor samples and the volume fraction of collected particulate matter explained by the source or source cluster to which the marker(s) or pattern can be attributed.

CONCLUSIONS

Direct TD-GC/MS analysis of 1- to 2-hr QF filter samples provides a rapid approach to characterization and identification of organic PM components in receptor as well as source samples.

Size-distributed particle concentration measurements, obtained in parallel with PM filter sampling, are presented as an in-situ, real-time calibration alternative to conventional filter weighing procedures.

Differential profiling of ambient source plume samples, in conjunction with size-distributed particle concentration measurement, is proposed as a low cost, minimally intrusive method of obtaining characteristic PM emission profiles of complex or inaccessible sources or source clusters.

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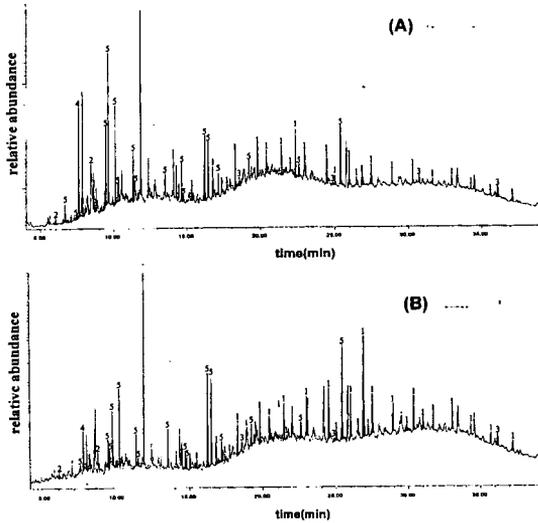


Figure 1. Comparison of solvent extracted (A) and thermally extracted (B) PM constituents. Peak labels: (1) alkanes; (2) N-containing compounds; (3) aromatics and PAH; (4) aliphatic alcohols and phenols; and (5) other O-containing compounds.

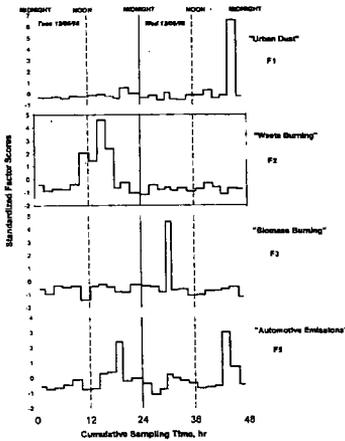


Figure 2. Time-resolved plot of four Varimax-rotated factor scores for the Hidalgo (TX) PM data set. All interpretations are tentative until confirmed by area-specific source sampling. Since factor scores are standardized a score of "3" can be regarded as a "3 σ event" in statistical terms, and so on. Note the characteristic periodic traffic peak pattern of F4 events and, the episodic character of major F1 and F2 events.

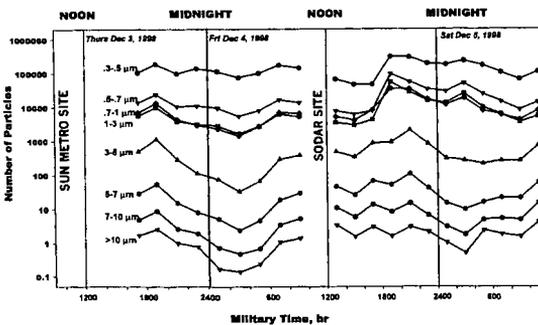


Figure 3. Averaged (2-hr averages of 4 min. intervals) 8-channel particle count at 2 El Paso (TX) sites. Note the "natural" division between the lower and higher size classes.

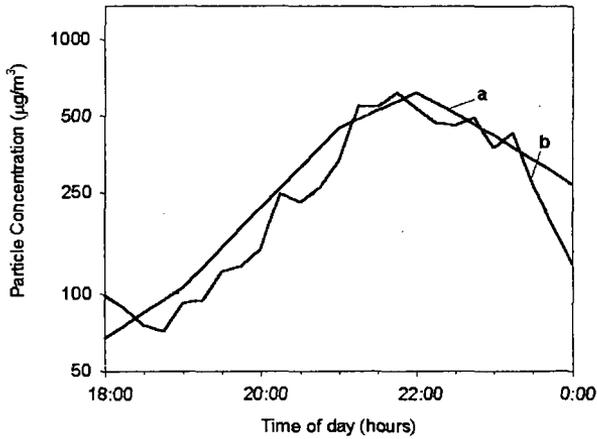
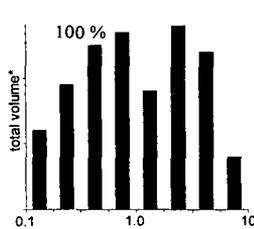
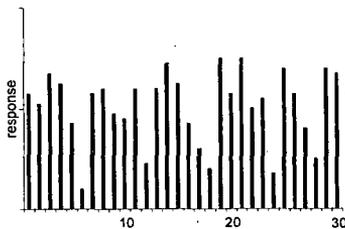


Figure 4. Use of beta attenuation monitor particle density measurements to calibrate particle density values calculated from multichannel particle count data at the Calexico site in December 1992.

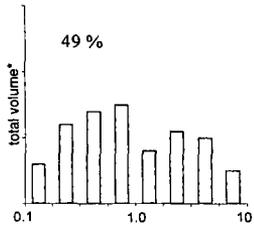
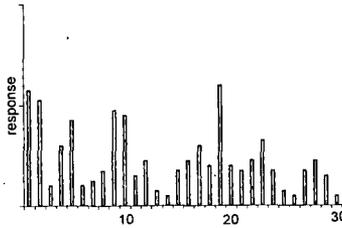
A. SOURCE PROXIMITY GRADIENT PROFILES (downwind)

c.g. Spectroscopic Data

Size / Volume Data



B. AMBIENT BACKGROUND PROFILES (upwind)



C. BACKGROUND-SUBTRACTED SOURCE PROFILES (A minus B)

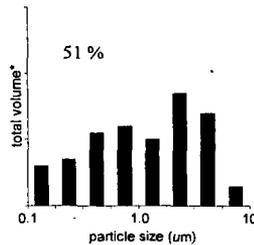
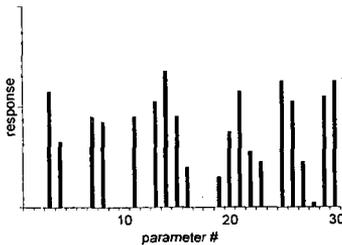


Figure 5. Conceptual illustration of the proposed Differential Source sampling approach aimed at producing characteristic, background-subtracted source profiles and the accompanying size-distributed particle data.

COMPOSITION OF THE ATMOSPHERIC AEROSOL AT THE POINT OF OBSERVATION

Bonne, G.P. and Mueller, P.K., Environment Division, Electric Power Research Institute, Palo Alto, CA.

Chen, L.W. and B.G. Doddridge, Departments of Chemical Physics and Meteorology, University of Maryland, College Park.

Butler, W.A., Potomac Electric Power Company, Washington, DC.

Zawadzki, P.A., Baltimore Gas & Electric Company, Baltimore, MD.

Chow, J.C, Kohl, S. and Tropp, R., Desert Research Institute, Reno, NV.

KEYWORDS: Particulate matter measurements, $PM_{2.5}$, aerosol equilibria

INTRODUCTION

It is difficult to avoid altering particulate matter suspended in the atmosphere with most particulate matter measurement techniques. We address the extent to which methods based on the separation of the particulate and gas phases adulterate the particulate phase in suspension at the point of sampling with respect to particles up to and including 2.5 μm in aerodynamic diameter ($PM_{2.5}$). Specifically, we consider mass alteration during sampling and subsequent sample processing due to the volatility of ammonium nitrate and organic matter, and due to the adsorption of organic compounds on quartz fiber filters.

Here we present results from sampling the ambient aerosol during July 1999 at Fort Meade, MD (39.083°N, 76.750°W), a non-urban site in the Baltimore-Washington corridor. Additional sampling will take place during the (ideally) seasonally representative months of January 2000, April 2000, July 2000, and January 2001 as part of the Maryland Aerosol Research and Characterization (MARCH-Atlantic) study, a multi-year project designed to facilitate improved understanding of atmospheric fine particulate matter. Specific objectives of the study are (1) to characterize the changes in composition of $PM_{2.5}$ as a function of time, (2) to identify the most likely sources of $PM_{2.5}$ to the region, (3) to investigate potential biases in various $PM_{2.5}$ measurement techniques, and (4) to provide useful information to the State of Maryland and EPA concerning PM measurements and regulations.

We add to the growing body of studies that have investigated potential sampling biases in filter based methods for particulate phase nitrates (e.g. Zhang and McMurry, 1992; Hering and Cass, 1999) and organics (e.g. Tang et al., 1994; Turpin et al., 1994; Gundel et al., 1995; Eatough et al., 1996). We compare the 24-hour TEOM $PM_{2.5}$ mass concentration with those measured by a collocated filter sampler, and examine how the $PM_{2.5}$ composition varied as a function of $PM_{2.5}$ mass concentration during July 1999. We also compare inorganic aerosol composition measurements to expectations based on aerosol thermodynamic equilibrium calculations.

EXPERIMENTAL

In July 1999, 24-hour filter samples for $PM_{2.5}$ concentration and composition along with gas phase HNO_3 , NH_3 and hourly measurements of SO_2 , CO and $PM_{2.5}$ were added to an existing state air quality monitoring site at Fort Meade, MD. The existing measurements consisted of 24-hour Federal Reference Method (FRM) for $PM_{2.5}$, 1-hour O_3 , NO, NO_x , and surface and aloft meteorology

This study employed two Sequential Filter Samplers (SFSs) and two Sequential Gas Samplers (SGSs) programmed to sample for 24 hours through filter packs that are replaced manually every third day. Detailed descriptions of these samplers can be found in Chow et al. (1996) and references therein. In brief, each sampler has two channels, each containing a filter pack containing one or two sampling filters through which a pump draws air at a rate of 20 L/min.

SFS-1 is used to determine $PM_{2.5}$ mass and chemical composition. The sampling stream to both channels of SFS-1 is preceded by a $PM_{2.5}$ size-selective inlet and nitric acid denuder. A Teflon filter is used on one channel to determine mass and elemental concentrations via gravimetry and x-ray fluorescence, respectively, after equilibration at $21.5 \pm 1.5^\circ\text{C}$ and $35 \pm 5\%$ relative humidity. The second channel contains a quartz filter followed by a sodium chloride impregnated cellulose filter. A section of the quartz filter is extracted and used to determine the concentration of water-soluble ions: sodium and potassium by atomic absorption spectroscopy; chloride, sulfate, and non-volatilized nitrate by ion chromatography; and ammonium by automated colorimetry. The sodium chloride impregnated cellulose filter is used to determine the

amount of particulate nitrate that evaporates off the front quartz filter. SFS-2 is used to determine the amount of organic (OC) and elemental (EC) carbon in $PM_{2.5}$. SFS-2 is equipped with sampling cartridges containing two quartz filters in series on one channel, and a Teflon filter followed by a quartz back-up filter on the second channel. A section of each quartz filter is analyzed by thermal optical reflectance (TOR) for organic and elemental carbon.

Gas phase nitric acid is sampled using SGS-1. Channel one contains a quartz filter followed by a sodium chloride impregnated cellulose filter. Channel two contains a nitric acid denuder upstream of the two filters. A section of every filter is extracted and analyzed for nitrate by ion chromatography. The ambient gas phase nitric acid concentration is determined from the difference between the total nitrate collected on the channel 1 filters minus the total nitrate collected on the channel 2 filters. A second SGS, SGS-2, is used to measure gas phase ammonia concentrations. One channel contains a quartz filter followed by a citric acid impregnated cellulose filter. The second channel contains an ammonia denuder upstream of the two filters. A section of each filter is extracted and analyzed for ammonium using automated colorimetry. The ambient gas phase ammonia concentration is determined from the difference between the total ammonium collected on the channel 1 filters minus the total ammonium collected on the channel 2 filters. The SFSs and SGSs were operated at ambient temperature.

The SFS and SGS filter packs are shipped cooled and sealed between a central laboratory and the sampling site approximately once each week. Filters are sealed and kept cold immediately after removal from the sampler. Each sampler contains a filter pack open to the atmosphere that is changed out every 3rd day. It serves as a dynamic blank, the variance of which determines the lower quantifiable limit for the respective observables.

Continuous measurements of $PM_{2.5}$ mass using a TEOM[®] Series 1400a (Patashnick and Rupprecht, 1991) equipped with a $PM_{2.5}$ inlet have been obtained at the site for all months after July 1999. The TEOM's sample stream of 3 L/min is preheated to 50°C prior to entering the sampling chamber.

RESULTS

The average 24-hour $PM_{2.5}$ concentration measured during July 1999 from SFS-1 was $20.6 \mu\text{g}/\text{m}^3$, with a range of 5.5 to $37.1 \mu\text{g}/\text{m}^3$. The 24-hour TEOM mass concentration averaged $3.5 \pm 1.2 \mu\text{g}/\text{m}^3$ higher (95% confidence interval, paired t-test) than the collocated SFS sampler. Measurements from the two samplers were tightly correlated with $R = 0.98$. On average, sulfate, ammonium, nitrate, organic carbon, elemental carbon, and crustal material composed 38%, 13%, 2%, 36%, 7%, 4% of $PM_{2.5}$ in July 1999 at Fort Meade, respectively. Substantial differences in the composition of $PM_{2.5}$ were observed between days with high and low $PM_{2.5}$ concentrations. On the days with the highest $PM_{2.5}$ concentrations ($>30 \mu\text{g}/\text{m}^3$, 8 days) in July 1999, the fraction in sulfate + ammonium averaged 59% ($19.6 \mu\text{g}/\text{m}^3$) of the total mass, while the fraction in carbonaceous material ($1.4 \cdot \text{OC} + \text{EC}$) averaged 27% ($8.9 \mu\text{g}/\text{m}^3$). The averages changed to 37% ($2.8 \mu\text{g}/\text{m}^3$) and 67% ($4.9 \mu\text{g}/\text{m}^3$), respectively, on the days with the lowest $PM_{2.5}$ concentrations ($<11 \mu\text{g}/\text{m}^3$, 7 days). Figure 1 displays how the composition of $PM_{2.5}$ varied with $PM_{2.5}$ concentration. It is apparent from Figures 1d and 1e that changes in the $PM_{2.5}$ concentration is driven largely by sulfate and ammonium rather than carbonaceous material.

The amount of nitrate collected on the backup NaCl impregnated cellulose filter in SFS-1 was approximately 9 times larger than the amount collected on the front quartz filter (Figure 2). Thus, evaporative losses of particle phase nitrate from quartz filters can result in a large underestimation of particulate nitrate in the eastern US in the summer. We assume that the nitrate collected on the backup filter represents the amount of ammonium nitrate that evaporated off the front quartz filter, which ranged from -1% to 9% (0.1 to $1.1 \mu\text{g}/\text{m}^3$) and averaged ~2% ($0.36 \mu\text{g}/\text{m}^3$) of the total $PM_{2.5}$ mass measured on the Teflon filter of SFS-1. If the Teflon filter is subject to the same evaporative losses of ammonium nitrate as the quartz filter, the $PM_{2.5}$ mass measurement may be underestimating the true ambient $PM_{2.5}$ concentration by 1 to 9% on any given day.

Potential biases associated with the organic particulate material may be larger. Each channel on SFS-2 employed the use of a quartz fiber back-up filter. One backup filter was preceded by a Teflon filter, while the other was preceded by a quartz filter. Figure 3 shows the amount of organic carbonaceous material that was detected on the backup filters, relative to what was measured on the front quartz filter of SFS-1. The amount of organic carbon measured on the backup filter behind the Teflon averaged over 50% of what was measured on the front quartz filter, while the backup filter behind quartz averaged ~30% of the OC measured on the front quartz filter. These amounts are on the order of 10% of the total $PM_{2.5}$ mass, indicating sampling biases associated with organic particulate material can be substantial in the eastern US in the summer. The material detected on the backup filters likely comes from two sources: 1) OC that evaporates off the front filters, which results in a negative sampling bias for OC and $PM_{2.5}$, and 2) gas phase organic compounds that adsorb on quartz filters, which contributes to a positive sampling bias for OC and the reconstructed mass. However, the relative contributions from each of these possibilities are highly uncertain. An additional source of uncertainty in the

determination of the concentration of organic particulate material resides in the multiplier of 1.4 used to estimate the average molecular weight of organic particulate matter (what actually resides on the filter) per carbon weight (what the TOR technique measures). The concentrations of organic particulate material reported here (as in Figure 1) were calculated by TOR analysis of the front quartz filters of SFS-2, without corrections from a backup filter.

We use the SCAPE2 (Kim et al., 1993) inorganic aerosol equilibrium model to compare the observed gas-particle partitioning of ammonia-ammonium and nitric acid-nitrate to calculations based on thermodynamic equilibrium. The SCAPE2 model requires inputs of observed temperature, relative humidity, total nitrate (gas + particulate phases), total ammonium, sulfate, sodium, chloride, potassium, and magnesium. The last four species are not significant in the data presented here. The model then calculates the gas phase concentrations of ammonia and nitric acid as well as the particulate phase concentrations of ammonium and nitrate at thermodynamic equilibrium. Figure 4 compares the SCAPE2 calculated and observed concentrations of the four species. The agreement between the equilibrium calculations and observations is excellent for the dominant phase species ($R \geq 0.99$ for gas phase nitric acid and particulate ammonium). The correlations for the minor phase species are not as strong. However, the differences between the SCAPE2 calculated and observed concentrations are not statistically significant at the 95% confidence level, except in the case of ammonia where the observed concentration is $0.11 \pm 0.07 \mu\text{g}/\text{m}^3$ larger (95% confidence interval) than the calculated concentration.

CONCLUSIONS

Based on measurements and theoretical evaluation of aerosol observations made in July 1999 at a non-urban site in the Baltimore-Washington Corridor, 24-hour $\text{PM}_{2.5}$ mass concentration measurements appear to underestimate the highest 20th percentile concentration of "dry" suspended particles by approximately 10%. This bias appears to be a function of losses of particulate ammonium nitrate and organics from the filters during sampling. Additional research is required to determine the sign and magnitude of the potential error in sampling organics.

Evaporative loss of particulate nitrate from filters during sampling can represent a large fraction of the total particulate nitrate. However, particulate nitrate appears to be only a small fraction of the total $\text{PM}_{2.5}$ in the Mid-Atlantic US in the summer. The observed partitioning of nitrate and ammonium between the particulate and gas phases is well reproduced by thermodynamic equilibrium theory.

Although the carbonaceous material accounts for approximately 20 to 70% of the $\text{PM}_{2.5}$ mass from the highest to the lowest mass concentration days, ammonium sulfate is the dominant constituent of the $\text{PM}_{2.5}$ on the higher mass concentration days.

Comparison of diurnal mass measurements of $\text{PM}_{2.5}$ using a TEOM instrument with a collocated 24-hour $\text{PM}_{2.5}$ filter sampler correlate with a small positive bias in the TEOM average over the filter sampler measurements.

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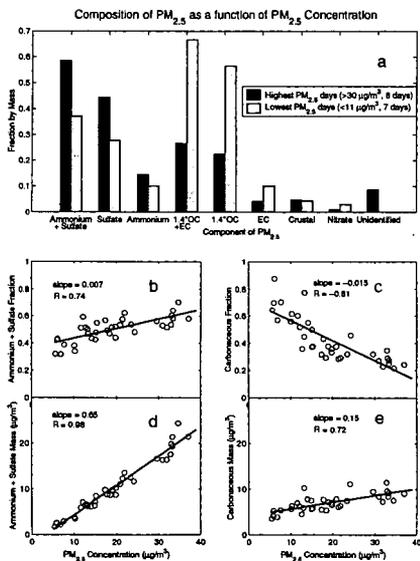


Figure 1. (a) Composition of PM_{2.5} on the days with the highest (>30 µg/m³, 8 days) and lowest (<11 µg/m³, 7 days) PM_{2.5} mass concentrations in July 1999 at Fort Meade, MD. The unidentified fraction represents the difference between PM_{2.5} measured on the Teflon filter of SFS-1 and the sum of sulfate + ammonium + 1.4*OC + EC + crustal + nitrate + volatilized ammonium nitrate. The crustal component is taken as 2.14*Si + 1.89*Al + 1.43*Fe + 1.67*Ti + 1.4*Ca + 1.2*K from x-ray fluorescence analysis. (b) The relationship between the fraction of PM_{2.5} in sulfate + ammonium and PM_{2.5} concentration. (c) The relationship between the fraction in carbonaceous material and PM_{2.5} concentration. (d) The relationship between the ammonium + sulfate mass and PM_{2.5} concentration. (e) The relationship between the carbonaceous mass and PM_{2.5} concentration. The carbonaceous material is determined from the front quartz filter of SFS-2, without corrections from a backup filter and is taken as 1.4*OC + EC.

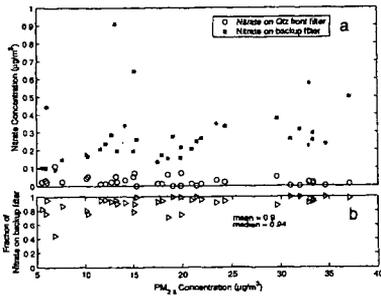


Figure 2. (a) The amount of nitrate collected on the front quartz filter and the backup sodium chloride impregnated cellulose backup filter in SFS-1 as a function of $PM_{2.5}$ concentration. (b) The fraction of nitrate collected on the backup filter ([nitrate on backup filter]/[nitrate on front filter + nitrate on backup filter]) versus $PM_{2.5}$ concentration.

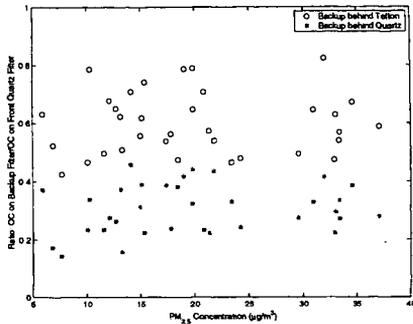


Figure 3. The amount of OC collected on each quartz backup filter in SFS-2 divided by the amount of OC measured on the front quartz filter of SFS-2 as a function of $PM_{2.5}$ concentration.

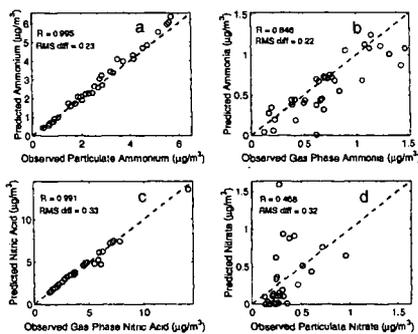


Figure 4. Comparison of the concentrations of inorganic $PM_{2.5}$ components calculated by the SCAPE2 aerosol equilibrium model to those observed for (a) particulate ammonium, (b) gas phase ammonia, (c) gas phase nitric acid, and (d) particulate nitrate. The dashed line is the 1:1 line. Observed particulate nitrate is taken as the sum of nitrate measured on the front quartz and backup sodium chloride impregnated cellulose filters of SFS-1. Observed particulate ammonium includes the ammonium that is assumed to have evaporated off the front quartz filter of SFS-1 in the form of ammonium nitrate, which is determined from the amount of nitrate collected on the backup sodium chloride impregnated cellulose filter.

PM_{2.5} SAMPLING AND CHARACTERIZATION PROGRAM IN LIBRARY, PA

S. D. Brandes, V. B. Conrad, S. E. Winter, J. A. Withum, D. S. Krofcheck
CONSOL R&D
4000 Brownsville Road
Library, PA 15129

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INTRODUCTION

Particles with a mean aerodynamic diameter of ca. 45 µm or less, known as total suspended particulate (TSP), have been of concern to the health community since the 1950s. In July 1997, the EPA proposed its most restrictive ambient air standard for particulate matter. This standard applies to particles with a mean aerodynamic diameter of 2.5 µm or less (PM_{2.5}). It sets an annual limit for PM_{2.5} of 15 µg/m³, averaged over three years, and a 24 h limit of 65 µg/m³ (98th percentile, averaged over three years). In supporting documentation for the recommendation to implement this new standard, EPA stated that SO₂ (a precursor to the formation of secondary sulfate particles) is a key source of PM_{2.5}, and of concern to human health. EPA also stated that the SO₂ is predominantly generated by the combustion of fossil fuels, especially coal. Another class of compounds which EPA stated to be a major component of PM_{2.5} and also of concern to human health is nitrates derived from NO_x generated in the combustion of fossil fuels. In addition to regulations based on alleged health effects, in an effort to regulate PM_{2.5}, EPA also proposed draft regional haze regulations that focus on the impact of PM_{2.5} on visibility impairment in Class I ("pristine") areas of the United States. The scientific bases for these standards are now under review.

CONSOL R&D began a sampling program in January 1997 in Library, PA (thirteen miles south of Pittsburgh, PA) to measure the concentration of PM_{2.5} particles collected from the air and to characterize the components of the collected samples. This paper describes the sampling methods, data collected, and conclusions drawn from this program.

At the time CONSOL began its sampling program, no federal reference method (FRM) had been established for the collection of fine particles 2.5 µm or smaller. At CONSOL, the initial samples were collected using cyclone samplers. CONSOL R&D has a great deal of experience using cyclones for the collection of particles from stationary source stack sampling work.

In July 1997, EPA published an FRM for PM_{2.5} collection; the method requires the use of impactors, not cyclones. CONSOL added a Graseby-Andersen FRM single channel sampler to the on-site PM_{2.5} sample collection effort being performed with the cyclones. Later, a Graseby-Andersen sequential PM_{2.5} sampler was employed. Collection with both the cyclones and the Graseby-Andersen samplers continued until January 1999, at which time the use of the cyclones was discontinued. The samplers were collocated (within four feet of each other). Weather data also were collected on the CONSOL Library, PA, site beginning June 1998.

EXPERIMENTAL

Prior to 1997, the procedures used to acquire samples with cyclone samplers were those used primarily for sampling of stack gases.¹ The cyclones used for this work provide a particle size cut (with a mean diameter of 2.5 µm, D₅₀) within the range of 0.1-10 µm.³ Two types of filter material were used, Teflon™ and quartz. Quartz filters are difficult to weigh because they fluctuate in weight with changes in humidity. However, they were used for selected samples to eliminate carbon background, which would interfere in the anticipated carbon analyses. Procedures for sample collection and determination of PM_{2.5} concentration with the FRM samplers is detailed in the Code of Federal Regulations 40 Part 50 Appendix L. The FRM specifies the use of Teflon™ filters. Field blanks were acquired; field blank weights are one to two orders of magnitude smaller than sample weights.

Collected samples were weighed and randomly selected samples were analyzed for sulfate, nitrate, chloride, and ammonium by ion chromatography (IC). Quartz filters were reserved for carbon analyses.

RESULTS AND DISCUSSION

Comparison of Cyclone to FRM Sampler Collected Filter Samples

Two cyclones were collocated with the single-channel Graseby-Andersen FRM sampler for thirteen months. $PM_{2.5}$ concentrations were calculated from the mass of particles collected on the filters and the air flow rate through the filters. Figure 1 shows good correlations ($R^2 = 0.967$ and $R^2 = 0.942$) between the $PM_{2.5}$ concentrations measured in the same 24 h period using the two sample collection devices. The slopes of the two lines on Figure 1 are 0.96 and 1.07 for cyclones 1 and 2, respectively.

Seasonal and Daily Variations

$PM_{2.5}$ concentrations for all samples collected outdoors in the period of January 1997 through August 1999 are shown in Figure 2. Some variations with the seasons can be observed. The $PM_{2.5}$ concentration in ambient air averages $20.0 \mu\text{g}/\text{m}^3$ throughout the two and one half plus years of the outdoor sampling program, excluding high ozone days. Ozone action days (designated as open points) were declared by the Pennsylvania Department of Environmental Protection (DEP). The average $PM_{2.5}$ concentration for high ozone days was $42.3 \mu\text{g}/\text{m}^3$. $PM_{2.5}$ concentrations were examined for variations according to day of the week (Table 1). Because of the large standard deviations, little variation is observed. The range of $PM_{2.5}$ concentrations is roughly equivalent regardless of the day of the week.

Variations in $PM_{2.5}$ Concentration with Weather Data and Ozone Concentration

Total $PM_{2.5}$ concentration was examined as a function of weather data (temperature, barometric pressure, rainfall, and humidity). A trend with weather data is evident only in the relationship of $PM_{2.5}$ and temperature. $PM_{2.5}$ concentration is higher on days when the temperature exceeds 80°F . The $PM_{2.5}$ concentration distribution shifts to higher values for samples acquired at $\geq 80^\circ\text{F}$ (Figure 3).

$PM_{2.5}$ concentrations are plotted as a function of ozone concentrations acquired by the Pennsylvania State DEP at a location 17 miles southeast of Library, PA (Charleroi, PA). $PM_{2.5}$ concentrations increase with increasing ozone concentration (Figure 4); this is consistent with the work of Chu and Cox². It cannot be definitively determined from these data whether the higher $PM_{2.5}$ concentration levels are a result of higher temperature, the higher ozone concentrations, or other confounding effects.

$PM_{2.5}$ Composition

Sixty-four filter samples collected from January 1997 through August 1998 were analyzed for sulfate, nitrate, ammonium, and chloride. The average composition for particles collected on non-ozone action days is: 32 wt % sulfate, 11 wt % ammonia, 7.5 wt % nitrate, 3.0 wt % chloride and 46 wt % organic and inorganic carbon and mineral matter. The average composition for samples collected on ozone action days is: 48 wt % sulfate, 14 wt % ammonia, 1.5 wt % nitrate, 2.2 wt % chloride, and 34 wt % carbon and mineral matter (Table 2).

The concentration of sulfate ($\mu\text{g}/\text{m}^3$) in the $PM_{2.5}$ collected on non-ozone days was in the range of 0.8 to $16.0 \mu\text{g}/\text{m}^3$. On ozone action days, the range of $PM_{2.5}$ sulfate concentrations was 7.4 to $35.5 \mu\text{g}/\text{m}^3$. There is a general increase in sulfate and ammonia concentration in the summer months and an apparent decline in concentration of nitrates. The highest chloride concentrations were found in particles collected in June and July.

Sulfates and nitrates exist in the atmosphere as aerosols. When reacted with ammonia, they form fine particles that can precipitate. Thus, the form of the sulfates and nitrates in the particles is likely to be ammonium salts. Several ammonium salts are possible (ammonium sulfate, $(\text{NH}_4)_2\text{SO}_4$, ammonium bisulfate, $(\text{NH}_4)\text{HSO}_4$ and ammonium nitrate, NH_4NO_3). In addition, chlorides would likely be found as ammonium chloride (NH_4Cl). The correlation between the concentration ($\mu\text{mole}/\text{m}^3$) of ammonium and the concentration ($\mu\text{mole}/\text{m}^3$) of sulfate in the $PM_{2.5}$ collected on all days is good ($R^2 = 0.94$). The ammonium and sulfate mole ratios may provide a clue to which ammonium sulfate salt predominates in the particulate matter. Two assumptions were made in the data analysis; they are: 1) all Cl^- and NO_3^- are present as ammonium salts, and 2) all SO_4^{2-} is present as an ammonium salt. The mole ratios of NH_4^+ (residual) to SO_4^{2-} , after accounting for the Cl^- and NO_3^- , range from -0.2 to 2.0. The average value is 1.3. Thirty-nine percent of the filter samples have an $\text{NH}_4^+/\text{SO}_4^{2-}$ ratio of 1.6 to 2.0 and 47% have a ratio of 1.0 to 1.5. From the limited number of samples and the limited data analysis, it is likely that both ammonium sulfate and ammonium bisulfate are present in the particulate matter.

CONCLUSIONS

A fine particle matter ambient air sampling program has been conducted on the CONSOL R&D sit in Library, PA, (south of Pittsburgh, PA) for almost three years. Particles with an aerodynamic mean diameter of 2.5 μm or less ($\text{PM}_{2.5}$) were collected using two types of sampling equipment, cyclones, and impactors. The two kinds of sampling equipment when collocated were found to collect the same mass of particles in the same time. The collected samples were analyzed using several methods. In conjunction with the particulate matter collection, weather data also were obtained for a portion of the sampling program duration. Total $\text{PM}_{2.5}$ concentration was found to vary slightly with season and vary little with day of the week, changing significantly (greater than one standard deviation from the mean of the non-ozone days) only on days of high ambient air ozone concentrations and temperatures greater than 80 °F. The magnitude of the effect of either of these linked variables on the concentration of $\text{PM}_{2.5}$ cannot be determined from the data presented here. However, because the effect is strong, the importance of including these and other confounding variables in $\text{PM}_{2.5}$ ambient air studies and $\text{PM}_{2.5}$ related health effect studies is indicated. The average $\text{PM}_{2.5}$ ambient air concentration for all days in which samples were acquired is 20.0 $\mu\text{g}/\text{m}^3$. On non-ozone action days, the average $\text{PM}_{2.5}$ concentration is 17.8 $\mu\text{g}/\text{m}^3$. Neither of these concentrations would meet the proposed EPA limit of 15 $\mu\text{g}/\text{m}^3$. The concentration of sulfate found (on average) for all days (33%) is approximately that found by EPA (34.1%) in $\text{PM}_{2.5}$ acquired in the eastern U.S.³ Further studies, which include compositional analyses of many more samples collected from sites around the eastern U.S., are required to confirm this result. A good correlation was found between the ammonium and sulfate concentrations in the particles indicating the possibility that the sulfate is resident in the particles as ammonium salts.

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Table 1. $\text{PM}_{2.5}$ Concentration Ranges, Averages, and Standard Deviations for Non-Ozone Action Days, Sorted by Day of the Week

	Number of Samples	Range		Avg	Std Deviation
		Low	High		
Monday	25	8.0	48.9	18.6	11.7
Tuesday	48	2.4	38.5	14.2	8.5
Wednesday	41	10.1	51.3	19.2	7.9
Thursday	75	2.3	46.9	18.6	8.1
Friday	12	5.9	28.4	17.2	6.5
Saturday	25	7.2	33.5	15.5	8.1
Sunday	26	6.2	34.7	18.6	8.4

Table 2. Average Concentration (wt %) of Components in $\text{PM}_{2.5}$ Samples

Component, wt %	All Samples (a)		Non-Ozone Action Days (b)		Ozone Action Days (c)	
	average	σ	average	σ	average	σ
Sulfate	33	13	32	12	48	7.9
Ammonium	11	3.2	11	3.3	14	2.0
Nitrate	7.0	19	7.5	20	1.5	1.3
Chloride	2.9	3.9	3.0	4.0	2.2	1.1
Balance (d)	46		46		34	

a) Total of all samples analyzed: 63

b) Total of non-ozone action day samples analyzed: 54

c) Total of ozone action day samples analyzed: 9

d) Includes Inorganic and Organic Carbon and Minerals

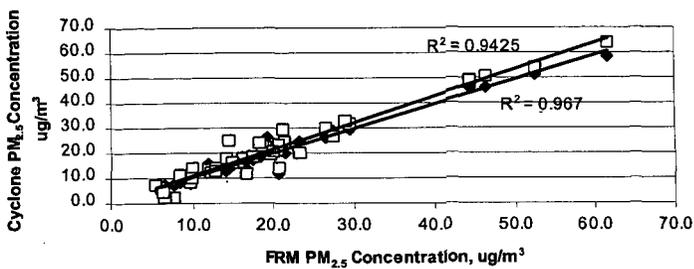


Figure 1. Comparison of PM_{2.5} Concentration Measured in Cyclones 1 (solid points) and 2 (open points) with the Single-Channel FRM Sampler.

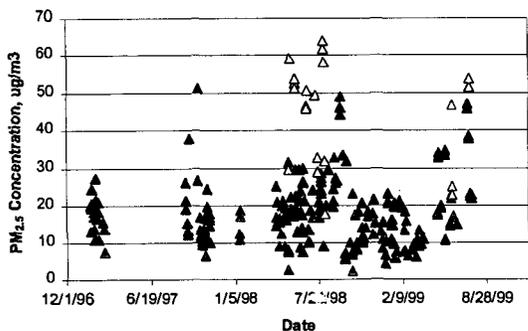


Figure 2. PM_{2.5} Concentration - CONSOL R&D Library, PA 1/27/97 - 7/30/99 (Open Points are Ozone Action Days).

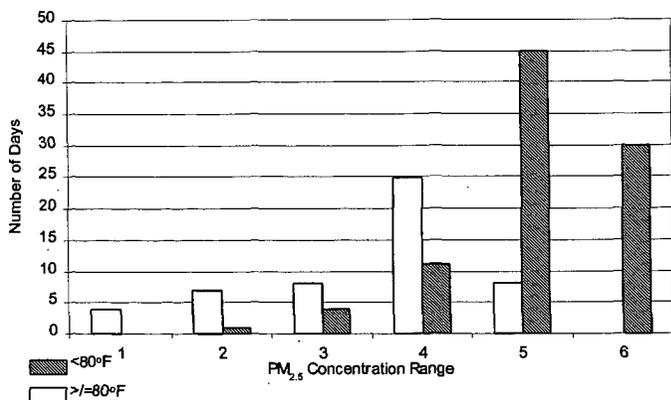


Figure 3. Change of PM_{2.5} Concentration Distributions with Different Outside Daily High Temperature Ranges.
 (PM_{2.5} Concentration Ranges (µg/m³): 1 = 50*; 2 = 40-50; 3 = 30-40; 4 = 20-30; 5 = 10-20; 6 = 0-10)

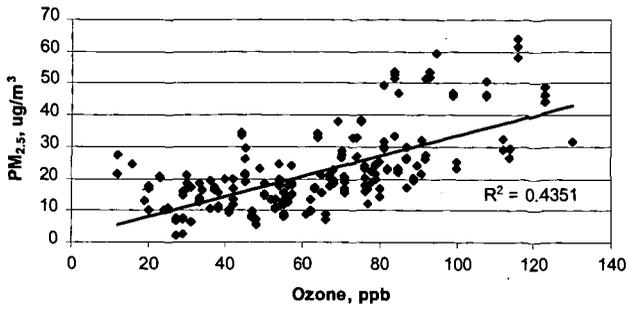


Figure 4. PM_{2.5} Concentration Measured in Library, PA vs. Ozone Concentration Measured in Charleroi, PA