

A52C MCC: Hall D Friday 1330h**EPA PM Supersite Program: Results and Findings From the Summer 2001 Field Intensive Posters****Presiding: K L Demerjian**, University at Albany**A52C-0123 1330h POSTER****Preliminary results from the Pittsburgh Air Quality Study**Spyros N. Pandis¹ (spyros@andrew.cmu.edu)Cliff I. Davidson¹ (cliff@andrew.cmu.edu)Allen L. Robinson¹ (alr@andrew.cmu.edu)Andrey Y. Khlystov¹ (andrey@andrew.cmu.edu)¹Carnegie Mellon University, Dept. of Engineering and Public Policy, Pittsburgh, PA 15213, United States

The Pittsburgh Air Quality Study (PAQS) is a collaborative effort among 20 research groups, and is part of the EPA Supersite Program. In collaboration with several other Supersites around the country, PAQS is also one component of an intensive experiment conducted in July 2001. The PAQS study includes monitoring for aerosol number, surface, and volume distributions, PM mass in several size ranges, single particle chemical composition, continuous aerosol sulfate, nitrate, and carbon mass, bioaerosols, hygroscopic aerosol growth, and filter-based aerosol chemical composition including trace metals, anions/cations, elemental and organic carbon, and various organic compounds. Meteorological data and concentrations of several trace gases are obtained simultaneously.

The results will be used to test a variety of hypothesis on atmospheric aerosols. Examples include our ability to account for aerosol mass by summing contributions of individual chemical species, the extent to which single particle chemical composition data can be used to determine bulk chemical concentrations, our ability to predict natural and anthropogenic sources of aerosols, and the extent to which aerosols contribute to increased morbidity and mortality in Pittsburgh. This paper summarizes a few of the interesting results obtained during the study, such as closure of the aerosol mass balance, frequent new particle formation, aerosol water content and artifacts when sampling carbonaceous aerosol.

A52C-0124 1330h POSTER**Fine Aerosol Composition and Radiative Effects in the Baltimore-Washington Corridor: Findings From the 2001 Summer Intensive**L.-W. Antony Chen¹ (775-674-7028; antony@meto.umd.edu)Bruce G. Doddridge² (301-405-7628; bruce@atoms.umd.edu)Russell R. Dickerson² (301-405-5364; russ@atmos.umd.edu)Judith C. Chow¹ (judyc@dri.edu)Brent N. Holben³ (brent@aeronet.gsfc.nasa.gov)¹Atmospheric Science Division, Desert Research Institute, 2215 Raggio Parkway, Reno, NV 89512²Department of Meteorology, University of Maryland, University of Maryland, College Park, MD 20742³Biospheric Sciences Branch, NASA Goddard Space Flight Center, NASA Goddard Space Flight Center, Greenbelt, MD 20771

Chemically speciated PM_{2.5} and trace gases were measured at Fort Meade (FME: 39.10°N, 76.74°W; elevation 46 m MSL) during summer 2001 (6/30 through 8/3) as a continuous effort of the Maryland Aerosol Research and Characterization study. FME is suburban and within 30 km south of the urban Baltimore supersite. 24-hr PM_{2.5} mass ranged from 2.1 to 29.5 μg m⁻³. Major species, by average mass fraction, includes sulfate (37%), organic matter (27%), ammonium (13%), elemental carbon (6%), nitrate (3%), and crustal material (3%). Reconstructed PM_{2.5} mass, calculated by summing the major species, is generally less than the gravimetric mass but within 10% difference. Visible extinction coefficient (*b_{ext}*) was recorded by an Automated Surface Observing System at the Baltimore Washington International Airport and column aerosol optical depth (AOD) by sun radiometers at the Goddard Space Flight Center to evaluate the conditions of regional haze. Both detectors were located within 20 km from FME. The correlation (*r*²) between 24-hr *b_{ext}*

and PM_{2.5} is low at 0.25 but increases to 0.51 when the aerosol water content, estimated using an aerosol thermodynamic modal ISORROPIA, is taken into account. Water contributed significantly on hazy days. This correlation suggests a mass extinction efficiency of ~ 9 m² g⁻¹. The hourly AOD at 500 nm was highly correlated with *b_{ext}* in the early morning and late afternoon (*r*² ~ 0.9) but not during mid-day hours (*r*² ~ 0.3) when *b_{ext}* is generally lower. This result, along with aircraft and ground lidar measurements, implies aloft fine aerosol mass in mid-day and a potentially stronger radiative forcing for the urban corridor.

A52C-0125 1330h POSTER**Atmospheric Boundary Layer Extinction Coefficient from the 2001/2002 Baltimore PM Supersite Experiments**Mariana Adam¹ (410-516-4483; mariana@jhu.edu)Markus Pahlow¹ (410-516-4483; mpahlow@jhu.edu)John Ondov² (jondov@wam.umd.edu)Michael E Thomas³ (Mike.Thomas@jhuapl.edu)Marc B Parlange¹ (parlange@jhu.edu)¹The Johns Hopkins University, Department of Geography and Environmental Engineering 3400 N Charles St, Baltimore, MD 21218, United States²University of Maryland, Department of Chemistry and Biochemistry, College Park, MD 20742, United States³The Johns Hopkins University - Applied Physics Laboratory, 11100 Johns Hopkins Road, Laurel, MD 20723, United States

During the 2001/2002 Baltimore PM Supersite field campaigns a series of instruments to measure atmospheric boundary layer (ABL) properties have been deployed at both urban and industrial sites. In this presentation we will focus on the analysis of data collected with an elastic backscatter lidar system, a spectroradiometer, a nephelometer, an APS (Aerodynamic Particle Sizer), a SMPS (Scanning Mobility Particle Sizer) and supporting meteorological data. The two remote sensing techniques lidar (active) and spectroradiometer (passive) allow one to obtain estimates of the extinction coefficients. We will present a comparison of techniques to determine profiles of the extinction coefficient based on these observations.

A52C-0126 1330h POSTER**Observations of OH, HO2 and OH Reactivity during PMTACS-NY2001: Comparison of Calculations and Observations**Xinrong Ren¹ (1-814-863-8752; ren@essc.psu.edu);Angelique Olliger¹ (aco111@psu.edu); HartwigHarder¹ (harder@mpch-mainz.mpg.de); MonicaMartinez¹ (martinez@mpch-mainz.mpg.de);Robert Leshner¹ (lesher@essc.psu.edu); JamesSimpas¹ (simpas@essc.psu.edu); William Brune¹

(1-814-865-3286; brune@essc.psu.edu)

¹Department of Meteorology, Pennsylvania State University, 503 Walker Building, University Park, PA 16802, United States

Hydroxyl (OH) and hydroperoxyl (HO2) radicals (collectively called HOx) were measured by a laser-induced fluorescence (LIF) instrument during the PM2.5 Technology Assessment and Characterization Study-New York (PMTACS-NY) summer 2001 intensive campaign in New York City. Measurement results for about one month were presented. Diurnal cycles of OH and HO2 show that the daytime maximum concentrations were 0.2-0.8 pptv and 2-22 pptv, respectively. Relatively high OH and HO2 persisted into early evening and were frequently observed during nighttime. This observation suggests that HOx chemistry may play an important role in the nighttime oxidation processes in the polluted urban atmosphere. The observed OH and HO2 concentrations were compared with those calculated by a box model that used RACM and was constrained to the ancillary measurements. For HO2, the observed concentration levels and variations were usually well reproduced by the model calculations, with a model to observation ratio of 0.85 on average for day and night. For OH, the model was generally able to match the measurement during daytime with a model to observation ratio of about 0.89, while the calculations significantly underestimated OH during nighttime. The budgets of HOx show that primary HOx production was dominated by the photolysis of HONO during daytime due to relatively high HONO concentrations, while nighttime HOx were primarily from the O3 and NO3 reactions with alkenes. The OH reactivity measurements agreed well with the calculations for both composite

diurnal variation and individual days. Calculations indicate that the reactions of OH + NO2, OH + hydrocarbons, OH + CO, and OH + NO accounted for about 32%, 25%, 12% and 10% of total OH loss, respectively, in this urban area.

A52C-0127 1330h POSTER**Characterization of Extractable Organic Fine Particulate Matter in the Atmosphere of Houston and Source Apportionment Calculations Using Organic Molecular Markers**Matthew P Fraser¹ (713-348-5883; mpf@rice.edu)Zhiwei W Yue¹ (zwyue@rice.edu)Birnur Buzco¹ (birnur@rice.edu)¹Rice University, Department of Civil and Environmental Engineering 6100 Main Street, Houston, TX 77005, United States

Samples of atmospheric PM2.5 were collected in Houston, TX every second day during the summer of 2000 as part of the EPA sponsored Houston Fine Particle Matter Supersite program. Sampling occurred at three sites, including one industrial location (HRM-3), one suburban location (Aldine) and one coastal location (La Porte). Twenty samples collected over a 24 hour period have been analyzed to quantify the concentration of 95 individual organic compounds, including: n-alkanes (C20 to C36), aromatic hydrocarbons (PAHs), n-alkanoic acids (C5 to C34), n-alkenoic acids (C18:1 and C18:2), carboxylic diacids (C3 to C10), petroleum biomarkers and others. As a whole, the extractable compounds were dominated by acids, especially by octadecanoic acid and hexadecanoic acid. The measured concentration of n-alkanes exhibited a peak at C29, with carbon preference index (CPI) values in the range of 0.97 to 2.0.

Using organic molecular markers, including seven alkanes, four petroleum biomarkers, seven PAH, one alkanolic acid, one alkenoic acid, levoglucosan, and three chemical components (Al, Si and Elemental Carbon), Chemical Mass Balancing (CMB) calculations have been performed on the ambient speciation data. These calculations are used to determine the contribution of seven different primary emission sources including: diesel powered vehicles, gasoline vehicles, wood combustion, fuel oil combustion, road dusts, meat cooking and vegetation waxes. The contribution of diesel powered vehicles and gasoline powered vehicles are the most important primary sources at all three sampling locations, with road dusts important at the industrial location. Meat cooking emissions were significant at all three locations. Wood combustion is an important contribution during a four-day period when uncontrolled wildfires in eastern Texas and Louisiana brought biomass combustion aerosols into the sampling region.

A52C-0128 1330h POSTER**PM2.5 Technology Assessment and Characterization Study in New York City PMTACS-NY: The 2001 Summer Field Intensive in Queens, NY**Kenneth L. Demerjian¹ (518-437-8705; kld@asrc.cestm.albany.edu)

James J. Schwab (518-437-8754; schwab@asrc.cestm.albany.edu)

Garland G. Lala (518-437-8703; lala@asrc.cestm.albany.edu)

¹ASRC University at Albany SUNY, 251 Fuller Road, Albany, NY 12203, United States

In the summer of 2001, an intensive field measurement campaign was carried out in Queens, NY as part of the PM2.5 Technology Assessment and Characterization Study in New York City (PMTACS-NY) to characterize the physical and chemical composition of particulate matter and related precursors utilizing conventional and advanced instrumentation technologies. The measurement program, involving a team of scientists from federal, state, university and private sector organizations, was designed to provide detailed time resolved chemical and physical characterization of the urban PM2.5/co-pollutant complex in relation to the regional environment.

A summary of the chemical and meteorological data defining specific events during the field intensive is presented as are results addressing specific hypothesis designed around PMTACS-NY program objectives. These include initial findings and conclusions related to 1) performance testing and evaluation of emerging measurement technologies and comparison with EPA mandated PM federal reference methods currently operational as part of the New York State and national PM2.5 monitoring network; 2) emissions characterization of CNG, standard diesel and CRT (Continuously Regenerating Technology) diesel retrofit powered vehicles; and 3) compositional comparisons of urban and regional PM2.5.

A52C-0129 1330h POSTER

Measurement of Ambient Aerosol Composition Using an Aerosol Mass Spectrometer: New York 2001 Supersite Summer Intensive Study

Frank Drewnick¹ (518-437-8715; drewnick@asrc.cestm.albany.edu)

James J. Schwab¹ (schwab@asrc.cestm.albany.edu)

Kenneth L. Demerjian¹ (kld@asrc.cestm.albany.edu)

¹Atmospheric Sciences Research Center, University at Albany, State University of New York, 251 Fuller Road, Albany, NY 12203, United States

A summer field measurement campaign in Queens, New York during July 2001 was operated as part of the PM_{2.5} Technology Assessment and Characterization Study in New York (PMTACS-NY) Supersite program. During this study several state-of-the-art aerosol instruments were deployed including an Aerosol Mass Spectrometer (AMS, Aerodyne Research, Inc.). This AMS is designed to deliver quantitative information on mass loadings and size-resolved mass distributions of volatile and semi-volatile aerosol chemical species.

AMS aerosol mass concentration measurements made during the campaign indicated significant contributions of sulfate and organic species to the total aerosol mass concentration. Sulfate, ranging from 0.05 $\mu\text{g}/\text{m}^3$ for clean days to 53 $\mu\text{g}/\text{m}^3$ for the most polluted period, had a median concentration of 2.6 $\mu\text{g}/\text{m}^3$. The total organics mass concentration, with a median mass concentration of 2.7 $\mu\text{g}/\text{m}^3$, ranged from 0.5 $\mu\text{g}/\text{m}^3$ up to 29 $\mu\text{g}/\text{m}^3$. In addition species-resolved size distribution measurements for sulfate, nitrate and organic aerosol particles indicate that sulfate and nitrate occur mainly internally mixed while the organic particles show a completely different size distribution, reflecting their different sources.

AMS mass concentration measurements combined with total aerosol mass concentration data from a co-located TEOM are used to provide a continuous mass balance with 10-min time resolution. Diurnal patterns of absolute sulfate, nitrate and organics mass concentration as well as diurnal patterns of relative contributions of different types of organic particles are calculated using the AMS mass concentration data. Typical size distributions as well as the evolution processes of particulate sulfate size distributions are presented, measured during high background concentrations of organic particles. In addition, capabilities and limitations of the AMS instrument, as indicated by laboratory testing and evaluation studies in the laboratory and in the field will be discussed.

A52C-0130 1330h POSTER

Mobile Particulate Emission Measurements of New York City Transit Buses and Other in use Vehicles

John T Jayne¹ (978-663-9500; jayne@aerodyne.com);

Manjula Canagaratna¹ (mrcana@aerodyne.com);

Scott Herndon¹ (herndon@aerodyne.com); Joanne

Shorter¹ (shorter@aerodyne.com); Mark

Zahniser¹ (mz@aerodyne.com); Charles Kolb¹

(kolb@aerodyne.com); Leah Williams¹

(williams@aerodyne.com); Doug Worsnop¹

(worsnop@aerodyne.com); Frank Drewnick²;

Kenneth L Demerjian²; Thomas Lanni³

¹Aerodyne Research, Inc., 45 Manning Road, Billerica, MA 01821, United States

²University at Albany, ASRC, 251 Fuller Road, Albany, NY 12203, United States

³NYS Department of Environmental Conservation, 625 Broadway, Albany, NY 12233, United States

Emissions from both diesel and gasoline powered motor vehicles are a significant source of particulate (PM_{2.5}) and trace gas pollution, especially in urban environments. Emission characterizations of motor vehicles can be performed using a dynamometer but these studies make fleet characterization impractical. Few studies have been performed which characterize emissions from in-use vehicles using a mobile sampling platform.

This work describes application of new technology instrumentation for rapid (1-5 second) and real-time characterization of both gas and particulate emissions from in-use vehicles and is part of the PM_{2.5} Technology Assessment and Characterization Study in New York (PMTACS-NY). An aerosol mass spectrometer (AMS) and a tunable infrared laser differential absorption spectrometer (TILDAS) system were deployed on the Aerodyne Research mobile laboratory designed to chase target vehicles in and around the New York City area and measure their emissions under actual driving conditions. The AMS provides particle size and composition information for volatile and semi-volatile matter

(0.03 μm) while the TILDAS system was configured to measure NO, NO₂, CO, CH₄, SO₂ and formaldehyde. In addition to a global positioning system, an ELPI and a condensation particle counter, the mobile laboratory was also equipped with a Licor CO₂ monitor to allow emission indices to be computed for the targeted vehicles. Emission indices for both particulate and trace gases correlated with engine type are reported for a representative fraction of the NYC Metropolitan Transit Authority (MTA) bus fleet in an effort to characterize new emission control technologies currently implemented by the NYC MTA.

A52C-0131 1330h POSTER

Advances in Continuous Mass Measurement Technology: TEOM Mass Monitor at 30°C with a Nafion Dryer at Rural and Urban New York State Locations.

James J Schwab¹ (1-518-437-8754;

schwab@asrc.cestm.albany.edu)

Henry D Felton² (1-518-402-8502;

hdfelton@gw.dec.state.ny.us)

Jeffrey Ams³ (1-518-452-0067; jams@rpco.com)

John Spicer¹ (1-607-359-2846;

jspicer1@adelphia.net)

Kenneth L Demerjian¹ (1-518-437-8705;

kld@asrc.cestm.albany.edu)

¹Atmospheric Sciences Research Center, University at Albany, State University of New York, 251 Fuller Road, Albany, NY 12203, United States

²New York State Department of Environmental Conservation, Bureau of Air Quality Surveillance, 625 Broadway, Albany, NY 12233-3256, United States

³Rupprecht and Patashnick Co., Inc., 25 Corporate Circle, Albany, NY 12203, United States

The National Ambient Air Quality Standards (NAAQS) for particulate matter (both PM₁₀ and PM_{2.5}) are expressed in terms of mass concentrations in micrograms per cubic meter of air. While there is tremendous interest in measuring chemically speciated concentrations of PM, bulk mass concentration will clearly be the regulated quantity for the foreseeable future. With this in mind, it is critically important to establish the quality of data collected under current promulgated PM_{2.5} mass measurement techniques; to identify any significant sources of error associated with the techniques; as well as to evaluate newer technologies that are capable of measuring PM continuously and in real time.

The well-known problems inherent in the measurement of ambient particulate matter include evaporation (and condensation) of semi-volatile compounds from (or onto) the collection medium; and the condensation and adsorption of reactive gases from the atmosphere. Recent work quantifying the sources of artifact errors for the Federal Reference Method (Pang, et al., 2002a; 2002b) showed significant evaporative losses from FRM filters. Similar losses are observed for the TEOM mass monitor, where evaporation of material from the filter head occurs at the default sensor temperature setting of 50°C.

The TEOM SES (Sample Equilibration System) was developed to reduce the transient measurement errors reported by the TEOM instrument due to water vapor, the most abundant condensable gas in the atmosphere; and to allow instrument operation at temperatures lower than 50°C. The SES TEOM has been operated at a site in rural SW New York State (Addison, NY) for more than two years and at a site in Queens, New York City for more than a year. Each site also has a co-located standard TEOM (operated at 50°C without a Nafion dryer) and an FRM filter sampler. For these sites, the summer data from all three instruments agrees quite well, typically to better than 10%. Significant differences, on the order of 40% or more, are apparent during the winter months. We will present these year round data sets and draw conclusions on the status of continuous mass concentration measurements using the TEOM mass monitor.

Pang, Y., Eatough, N. L., Wilson, J., and Eatough, D. J. (2002a) Effect of Semivolatile Material on PM_{2.5} Measurement by the PM_{2.5} Federal Reference Method Sampler at Bakersfield, California. *Aerosol Sci. Technol.* 36:289-299

Pang, Y., Eatough, N. L., and Eatough, D. J. (2002b) PM_{2.5} Semivolatile Organic Material at Riverside, California: Implications for the PM_{2.5} Federal Reference Method Sampler. *Aerosol Sci. Technol.* 36:277-288

A52C-0132 1330h POSTER

Intercomparison and Evaluation of Semi-Continuous PM-2.5 Nitrate and Sulfate Instruments During PMTACS-NY Summer 2001 Campaign in New York City

Olga Hogrefe¹ (518-437-8722;

olga@asrc.cestm.albany.edu)

Frank Drewnick¹ (518-437-8715;

drewnick@asrc.cestm.albany.edu)

James J. Schwab¹ (518-437-8754;

schwab@asrc.cestm.albany.edu)

Henry D. Felton² (518-402-8502;

hdfelton@gw.dec.state.ny.us)

Kenneth L. Demerjian¹ (518-437-8705;

kld@asrc.cestm.albany.edu)

¹Atmospheric Sciences Research Center - University at Albany, 251 Fuller Rd., Albany, NY 12203, United States

²New York State Department of Environmental Conservation, 625 Broadway, Albany, NY 12233, United States

During the PM_{2.5} Technology Assessment and Characterization Study (PMTACS-NY) intensive measurement campaign in New York City (Queens) during Summer 2001, several semi-continuous PM-2.5 nitrate and sulfate instruments were deployed and operated side-by-side. The instruments were Rupprecht and Patashnick Ambient Particulate Nitrate Monitor (8400N) and Ambient Particulate Sulfate Monitor (8400S), an Aerodyne Research, Inc. Aerosol Mass Spectrometer (AMS), a Particle into Liquid Sampler with IC (PILS-IC) developed by Georgia Institute of Technology, and a Continuous Sulfate Monitor developed by George Allen at Harvard School of Public Health (HSPH). The performance of each of the instruments in the field is described briefly.

The intercomparison of the sulfate mass concentration measurements from the four semi-continuous instruments yields almost one-to-one correlation between four instruments with correlation coefficients (R^2) values above 0.9. The intercomparison of the nitrate measurements from the three semi-continuous instruments yields (R^2) values of approximately 0.9. The 8400N results are lower than the PILS-IC and AMS values. The AMS and PILS-IC mass concentrations agree within 10%.

Semi-continuous nitrate measurements are compared against one set of 24-hour filter samples analyzed by ion chromatography. Semi-continuous sulfate measurements are compared against three sets of 24-hour filter samples and one set of 6-hour filter samples. Semi-continuous particulate nitrate and sulfate measurements are highly correlated to the filter samples with (R^2) greater than 0.9. It appears that PILS and AMS nitrate measurements agree with the filter results to within 10%, while the 8400N nitrate mass concentration measurements are biased low by 33%. Comparison of semi-continuous particulate sulfate measurements with the filter measurements shows that the former are biased low by about 15%. Possible explanations for these biases will be discussed.

A52C-0133 1330h POSTER

COMPARISONS OF SPECIATED PM-2.5 MASS AT RURAL AND URBAN NEW YORK STATE LOCATIONS

Henry Felton¹ (1-518-402-8502;

hdfelton@gw.dec.state.ny.us)

Kevin Civerolo¹ (1-518-402-8402;

schwab@dec.state.ny.us)

James J Schwab² (1-518-437-8754;

schwab@asrc.cestm.albany.edu)

Kenneth L Demerjian² (1-518-437-8705;

kld@asrc.cestm.albany.edu)

¹New York State Department of Environmental Conservation, Bureau of Air Quality Surveillance, 525 Broadway, Albany, NY 12233-3256, United States

²Atmospheric Sciences Research Center, University at Albany, State University of New York, 251 Fuller Rd., Albany, NY 12203, United States

The EPA Speciation Monitoring program is designed to determine the concentrations of 58 compounds contributing to the composition of ambient atmospheric particles smaller than 2.5 microns at various locations. Typically, siting criteria favor areas representative of high population exposure and relatively strong local pollution sources. The New York State Department of Environmental Conservation; (NYSDEC) in conjunction with the New York PMTACS Supersite program has augmented the predominantly urban PM-2.5 speciation network with measurements at two rural monitoring sites. In addition to providing data well

suited to characterizing the composition of regional PM-2.5 air quality these sites provide the opportunity to compare filter based speciation data to measurements performed with the newest continuous speciation instrumentation technologies.

PM-2.5 chemical speciation samplers draw from 600 to 1000 liters of air per hour across three filters simultaneously over a 24 hour period. The three filters are subjected to specific lab analyses to determine the concentrations of targeted compounds; including metals, ions such as sulfate, nitrate, and ammonium, and elemental and organic carbon. Data from these sites are collected on a one day in three schedule and are available for a year or more from the various locations.

PM-2.5 speciation data are used to determine a ranking of compounds responsible for particulate pollution in various geographical locations in New York State. This information is useful in the attribution of sources to observed PM-2.5 concentrations and in the identification of the differences and similarities of these contributions in urban versus rural environments. PM-2.5 speciation data were obtained at two rural locations, Pinnacle State Park near Corning, NY and Whiteface Mountain in the Adirondacks; and at two urban locations, Rochester, NY and New York City, NY. Comparisons of the rural and urban measurement data suggest that compounds such as sulfate have distinct contributions from long range transport, while nitrate and organic carbon compounds indicate a pattern of more local generation, consistent with their overall atmospheric lifetimes. Back trajectory analysis has been applied to show the relationship between potential source regions and specific PM-2.5 species concentrations.

A52C-0134 1330h POSTER

Measurements of Natural Radioactivity in Submicron Aerosols in the Pittsburgh Area.

Nancy A. Marley¹ (630 252 5014; marley@anl.gov)

Jeffrey S. Gaffney¹ (630 252 5178; gaffney@anl.gov)

¹Argonne National Laboratory, Bldg. 203/ER 9700 S. Cass Ave., Argonne, IL 60439, United States

Natural radionuclides can be useful in evaluating the transport of ozone and aerosols in the troposphere. We have used natural radioactivity to estimate apparent residence times for submicron aerosols in the troposphere by looking at the disequilibrium of lead-210 with its daughters bismuth-210 (5-day half-life) and polonium-210 (138-day half-life). We have also measured the activity of beryllium-7 on fine aerosols to examine potential upper-air transport into the tropospheric boundary layer. Two sites in the Pittsburgh area during the summer of 2001 were sampled for beryllium-7, lead-210, bismuth-210, and polonium-210 on fine aerosols by using a Sierra Impactor (Stage 4) that allowed a nominal 1-micrometer cutoff diameter.

One site was located approximately 5 km east of downtown Pittsburgh, on a rooftop next to Schenley Park (40.4395° N latitude and 79.9405° W longitude, elevation 310 m). A second site was located at the U.S. Department of Energy National Energy Technology Laboratory (NETL) Ambient Air Monitoring Station, approximately 15 km south of downtown Pittsburgh (40.30655 deg N latitude and 79.9794 deg W longitude, elevation 325 m). At both sites, 24-hour samples were collected from July 22 to July 30, 2001. Nine samples were taken at the NETL site, and six were taken at the Schenley Park site. The method for determining the lead-210 and its daughters will be described briefly. Apparent residence times ranged from 10-46 days, with an average of 23 days. Data indicate that little wind-blown soil or dust affected the area during the study. The importance of fine aerosol transport will be emphasized.

The authors wish to thank Donald Martello of the NETL and Natalie J. Anderson of Carnegie Mellon University for sample collection. This work was supported by the United States Department of Energy, Atmospheric Chemistry Program.

A52C-0135 1330h POSTER

The contribution of secondary organic aerosol to PM2.5 concentrations in Pittsburgh

Juan C Cabada¹ (412 268 3650;

jcc@andrew.cmu.edu); Spyros N Pandis¹ (412 268 3135; spyros@andrew.cmu.edu); Allen L Robinson¹; R Subramanian¹; Andrea Polidori²; Barbara Turpin²

¹Carnegie Mellon University, 5000 Forbes Ave, Pittsburgh, PA 15213, United States

²Rutgers University, 14 College Farm Road, New Brunswick, NJ 08901, United States

A major component of PM2.5 in the Eastern US is carbonaceous material. This organic particulate matter results from both direct emissions from sources such as

automobiles, trucks and industries (primary), and from the oxidation of organic gases (secondary). Data from the Pittsburgh Air Quality Study are used to examine the contribution of secondary organic aerosol to the total organic aerosol loading measured in the city during 2001 and 2002. The contribution of secondary organic aerosol is estimated by using elemental carbon as a tracer for primary emissions of organic particulate matter (OC to EC ratio approach). A systematic method for the determination of the primary ratio has been developed based on the correlation of measurements of OC and EC to gaseous tracers of photochemical activity (O3) and primary emissions (CO, NOx). This method is applied to different sets of organic aerosols measurements (using an undenuded sampler, a denuded sampler and an in-situ carbon analyzer) for carbonaceous concentrations. Consistent results for the SOA fraction are obtained when the method is applied to the different sets of measurements for OC and EC. This approach indicates that between 20 and 40% of the organic particulate matter in Pittsburgh during the summer and fall of 2001 is secondary in origin while negligible contributions of SOA are estimated for the winter of 2001 and the spring of 2002.

A52C-0136 1330h POSTER

Measurement of Ambient Elemental Carbon Using the Thermal-Optical Transmittance Technique: Effect of Sample Volume and Refractory Loading on the OC/EC Split

R Subramanian¹ (1-412-268-8540; rs3@andrew.cmu.edu)

Andrey Y Khlstov² (andrey@andrew.cmu.edu)

Barbara J Turpin³ (turpin@aesop.rutgers.edu)

Allen L Robinson¹ (alr@andrew.cmu.edu)

¹Carnegie Mellon University, Mechanical Engineering, 5000 Forbes Ave, Pittsburgh, PA 15213, United States

²Carnegie Mellon University, Chemical Engineering, 5000 Forbes Ave, Pittsburgh, PA 15213, United States

³Rutgers University, Environmental Sciences, 14 College Farm Rd, New Brunswick, NJ 08901, United States

Ambient carbonaceous aerosols have been measured on a daily basis in Pittsburgh, PA for over a year. A discrepancy is observed when comparing ambient elemental carbon (EC) levels from samples collected over a 24-hour period to those measured at a higher frequency. For example, the 24-hr average EC calculated from 5 high frequency samples of 4 to 6 hour duration is on average a factor of 2 higher than the value determined from a simultaneous 24-hour sample.

It is well known that EC is operationally defined based on the analysis method, and that the results from different analytical methods do not agree. However, this is not an explanation for the observed discrepancy because all the samples were analyzed with a Sunset Labs Thermal-Optical Transmittance (TOT) analyzer. The TOT method corrects for the pyrolysis of organic carbon (OC) that occurs during analysis by measuring the transmittance of the filter. The ambient EC is taken as the mass of carbon that evolves after the transmittance returns to its original, pre-analysis value. The underlying assumption of the method is that either (a) the pyrolyzed carbon (PC) and ambient EC have similar optical properties, or (b) the PC comes off completely before the EC.

To better understand the cause of the observed discrepancy, experiments were performed involving washing of ambient samples with organic solvents (to reduce OC and minimize pyrolysis) followed by OC/EC analysis, and use of sucrose standards on filters with different refractory levels. Comparing the washed and unwashed filters shows that PC evolves at the same time as ambient EC, and further, that the optical transmittance of these two types of carbon are different. The refractory appears to have two effects on the thermal evolution of the aerosol carbon: (1) higher refractory content increases pyrolysis of the OC, and (2) the refractory causes light absorbing carbon (PC and EC) to come off earlier (at lower temperatures) in the analysis cycle. The net effect of the refractory is to alter the relative rate at which PC and EC evolve from the filter changing the OC/EC split assigned by the TOT technique.

A52C-0137 1330h POSTER

Monitoring of Water Content of Ambient Aerosol During the Pittsburgh Air Quality Study

Andrey Y Khlstov¹ (412-268-5778; andrey@andrew.cmu.edu)

Charles O Stanier¹ (cos@andrew.cmu.edu)

Dimitris Vayenas² (vay@terpsi.iceht.forth.gr)

Spyros N Pandis¹ (spyros@andrew.cmu.edu)

¹Dept. of Chemical Engineering, Carnegie Mellon University, 5000 Forbes Ave., Pittsburgh, PA 15213, United States

²Dept. of Environmental and Natural Resources Management, University of Ioannina, Agrinio 45110, Greece

The absorption of water by atmospheric particles affects air quality, visibility, climate, particle lifetime, and interactions with semi-volatile compounds. Often, the water content of aerosols is calculated by a thermodynamic equilibrium approach. Due to a lack of knowledge about hysteresis effects, aerosol homogeneity, and chemical interactions, there is significant uncertainty in estimates of water concentrations for continental tropospheric aerosols. To address this, aerosol size distributions measured at both dried and ambient relative humidities are being monitored at a sampling site in the Northeastern United States dominated by regional transport of sulfate- and organic-containing aerosols. Four ambient and four dry size distributions are measured each hour, along with a suite of gas-phase, particle-phase, and meteorological parameters. Here we report hourly observations of aerosol water content for over 3500 different hours spanning a wide range of relative humidities, temperatures, and aerosol compositions during a period of several months. The observations are compared with thermodynamic equilibrium calculations based on the simultaneously measured chemical composition data. The effects of organic compounds are evaluated by analyzing changes in water uptake with the fraction of organic compounds. The aerosol size distributions were measured by an automated in-situ system which conditioned aerosols at ambient and dry conditions using computer controlled valves and Nafion dryers. The system included two Scanning Mobility Particle Sizers (SMPS) and an Aerodynamic Particle Sizer (APS) which measured the aerosol size distribution between 5 nm and 10 μm in diameter.

URL: <http://homer.cheme.cmu.edu>

A52D MCC: 125 Friday 1330h Oxygenated VOCs I: From Emission to Abundance

Presiding: G W Schade, University of California, Berkeley; J de Gouw, NOAA Aeronomy Laboratory

A52D-01 1340h INVITED

OVOC Emissions and Atmospheric Transformations.

Robert J Yokelson¹ (4063294812;

byok@selway.umt.edu); Ted J Christian¹ (theo@selway.umt.edu); Isaac T Bertschi¹; Darold E Ward²; Richard J Field¹; Peter V Hobbs³; Jon Goode¹; Sherri Mason¹; Ron Susott²; Ron Babbitt²; Wei Min Hao²

¹Department of Chemistry, University of Montana, Missoula, MT 59812, United States

²USDA Forest Service, Fire Laboratory, PO Box 8089, Missoula, MT 59807, United States

³Department of Atmospheric Sciences, University of Washington, Seattle, WA 98195, United States

We quantified the main emissions from a few vegetation samples and many biomass fires using ground-based, open-path FTIR and airborne, closed-cell FTIR. The two instruments have been rigorously compared to each other and to PTR-MS and canister sampling. OVOC are major emissions from plants. OVOC account for about 70 percent of NMOC from savanna fires (the largest type of biomass burning) and 70-80 percent of NMOC from production and use of domestic biofuels (the second largest type of biomass burning). A table of average biofuel emissions is presented. Data from laboratory and free-burning fires, obtained from Alaska to South Africa, is used to develop equations that predict OVOC emissions from a wide variety of global fires. The impact of OVOC on smoke plume chemistry and the post-emission transformations of OVOC were investigated with two models. Addition of HCHO alone to the simple chemistry used in some global models dramatically reduces NOx lifetime and speeds up O3 formation rates in plumes. A detailed model verifies these effects and shows that OVOC profoundly affect formation of HOx, peroxide, and nitrogen reservoir species. The modeled photochemical transformations of OVOC are diverse, but some key pathways are unknown. We observed rapid production of both O3 and additional OVOC and OH of 1.7E7 in smoke plumes in Alaska and Africa; all reasonably consistent with model predictions. In addition, we found that cloud processing caused large post-emission changes in smoke trace gases